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Angular Group Induced Bond Alternation (AGIBA). Part IX. Interactions with the Pyrimidine Ring

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Angular Group Induced Bond Alternation (AGIBA). Part IX. Interactions with the Pyrimidine Ring[#]

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Abstract

Motivation. Angular groups attached to the aromatic rings cause an increase of the double bond localization called Angular Group Induced Bond Alternation (AGIBA). The effect for the groups with single bonds, X–Y, increases the double bond character of the s–*cis* CC bond in the ring, whereas the groups with double bonds, X=Y, work in the opposite direction, increasing the single bond character of the s–*cis* bond.

Method. The effect for pyrimidine ring is studied by use of the X–ray diffraction geometry of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine and optimized geometry of substituted in various positions vinylo, formylo, imino, nitroso and methoxy derivatives of pyrimidine optimized at B3LYP/6–311G** level of theory.

Conclusions. The AGIBA effect is less expressed in the pyrimidine derivatives compared to that observed for benzene derivatives.

Keywords. *Ab initio* calculation; substituent effect; pyrimidine.

Abbreviations and notations

AGIBA, angular group induced bond alternation	^{1}H NMR, proton nuclear magnetic resonance
CCDC, Cambridge Crystallographic Data Center	HOSE, harmonic oscillator stabilization energy

1 INTRODUCTION

Angular groups substituted to the monocyclic aromatic π electron systems like benzene or *s*–triazine cause substantial structural consequences [1–4] known as Angular Group Induced Bond Alternation (AGIBA) [5–7]. These effects, documented by both the experimental and computational studies [1–7] may be briefly presented as in Scheme 1. The single and double bonded groups cause shortening and lengthening of the s–*cis*–CC bond in the benzene ring, respectively.

The local structural changes are then propagated over the whole aromatic rings like benzene or *s*–triazine and are also observed in non–aromatic systems such as borazine and boraxine [8–9].

[#] Dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday.

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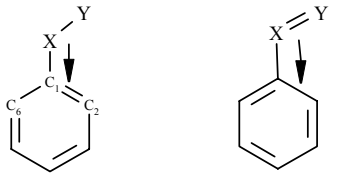
Usually the effect is described either by the difference between the C_1C_2 and C_1C_6 bond lengths (see Scheme 1), or conveniently by using the HOSE model [10–11] which allows us to estimate the weights of the canonical structures directly from the bond length of a molecule in question (or its fragment). Therefore the imbalance between two Kekulé structures of benzene manifests the AGIBA effect. For benzene derivatives the Kekulé structure imbalances for the whole ring and solely for the C_1C_2 and C_1C_6 bonds are practically the same [4].

Scheme 1. The phenomenological rule of the AGIBA effect



The geometry changes described above are the result of a superposition of at least two effects [4–5]:

(*i*) A σ electron one that is due to the partial rehybridization at the substituted carbon, which according to the Bent–Walsh rule [12–13] results from the increase of the bond angle XC_1C_2, which in consequence increases the *s*–contribution to the sp^2 orbital in the direction of bond C_1C_2 and makes the bond shorter. This is well known for benzene annelated with small rings and is often associated with the Mills–Nixon effect [14] Recently it has been nicely documented by X–ray determined structures [15] and also analyzed by computational experiments [16–20].

(*ii*) A through space π electron interaction between the double bonds in the X=Y group and the C_1C_2 bond in the ring leading to the lengthening of the latter bond [4]. This effect is sufficiently greater than (*i*) since despite of the XC_1C_2 bond angle usually greater than 120^o (and similar in value to those for X–Y substituted species), the C_1C_2 bond is found to be longer than C_1C_6 [5].

The purpose of this report is to answer the question how the above mentioned effect does operate in pyrimidine ring, *i.e*. how differ AGIBA acting on CN bonds which are more polarized than CC bonds in benzene. For this purpose a low temperature X–ray diffraction study of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine was performed. Additionally a high level *ab initio* optimization of 15 substituted derivatives of pyrimidine was carried out at the B3LYP/6–311G** level of theory.

2 EXPERIMENTAL DATA

2.1 Synthesis

(E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine was obtained along with 2,4–bis–[2–(4–methoxyphenyl)ethenyl]pyrimidine from 2,4–dimethylpyrimidine [21] and anisaldehyde

following the procedure reported for the preparation of 2,5–bis–[2–(4–methoxyphenyl)ethenyl]–pyrazine [22]. The chromatography of the crude reaction product on a column of alumina using 4:1 hexane/methylene chloride as an eluant gave (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine as the more polar component with 27% yield. Pale yellow needles from hexane/methylene chloride, m.p. 111 – 112 °C (uncorrected). ^{1}H NMR δ(ppm): pyrimidinylene: 8.54 (d, 1H, 6–H, J = 5.1Hz), 7.11 (d, 1H, 5–H, J = 5.1Hz), 2.74 (s, 3H, 2–CH_3); styryl: 7.54 (d, 2H, 2'–H; 6'–H, J = 8.7Hz), 6.93 (d, 2H, 3'–H; 5'–H, J = 8.7Hz), 3.84 (s, 3H, 4'–OCH_3), 7.77 (d, 1H, =CH, J = 16.0Hz), 6.92 (d, 1H, =CH, J = 16.0Hz); ^{13}C NMR δ(ppm): 168.04 (s), 162.76 (s), 160.67 (s), 157.15 (d), 136.65 (d), 2 ∗ 129.14 (d), 128.47 (s), 123.78 (d), 114.99 (d), 2 ∗ 114.33 (d), 55.37 (q), 26.24 (q). Anal.: Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 73.96; H, 6.24; N, 12.00.

The less polar pyrimidine derivative: 2,4–bis–[2–(4–methoxyphenyl)ethenyl]pyrimidine was obtained with 38% yield. Fragile, grayish–yellow plates from hexane/methylene chloride, m.p. 186 – 187°C (uncorrected). ^{1}H NMR δ(ppm): pyrimidinylene: 8.60 (d, 1H, 6–H, J = 5.2Hz), 7.07 (d, 1H, 5–H, J = 5.2Hz); 2–styryl: 7.60 (d, 2H, 2'–H, 6'–H, J=8.7Hz), 6.93 (d, 2H, 3'–H, 5'–H, J = 8.7Hz), 7.98 (d, 1H, =CH, J = 16.0Hz), 7.14 (d, 1H, =CH, J = 16.0Hz); 4–styryl: 7.56 (d, 2H, 2''–H, 6''–H, J = 8.7Hz), 6.93 (d, 2H, 3''–H, 5''–H, J = 8.7Hz), 7.84 (d, 1H, =CH, J = 15.8Hz), 6.94 (d, 1H, =CH, J = 15.8Hz); 3.84 (s, 6H, 4'–OCH_3, 4''–OCH_3); ^{13}C NMR δ(ppm): 164.91 (s), 162.66 (s), 160.66 (s), 160.38 (s), 157.18 (d), 137.38 (d), 136.58 (d), 2 ∗ 129.16 (d), 2 ∗ 129.10 (d), 128.99 (s), 128.54 (s), 125.65 (d), 123.93 (d), 115.16 (d), 2 ∗ 114.33 (d), 2 ∗ 114.23 (d), 55.37 (q), 55.34 (q). Anal.: Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.41; H, 5.86; N, 8.01.

Spectra. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity plus–200 in deuteriochloroform with TMS as internal standard at 200 and 50 MHz, respectively.

2.2 Crystal Structure Determination

Crystal data regarding the structure of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine together with the refinement details are given in Table 1. All measurements on the crystals were performed on a Kuma KM4CCD κ–axis diffractometer with graphite–monochromated MoKα radiation. The crystal was positioned at 62 mm from the KM4CCD camera 1000 frames were measured at 1.2° intervals with a counting time of 25 sec. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs.

The structure was solved by direct methods [23] and refined using SHELXL [24]. The refinement was based on F^2 for all reflections except those with very negative F^2. The weighted R factors wR and all goodness–of–fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2s(F_0^2)$ criterion was used only for calculating R factors

and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in [25]. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated with the deposition number CCDC 188432. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223)336–033; E–mail: deposit@ccdc.cam.ac.uk).

Table 1.

Empirical formula	$C_{14}H_{14}N_2O$
Formula weight	226.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions:	a = 26.482(5) Å b = 7.1550(14) Å c = 6.3070(13) Å β = 99.54(3)º
Volume	V = 1178.5(4) $Å^3$
Z	4
Calculated density	1.275 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	480
Crystal size	0.3 x 0.5 x 0.7 mm
Theta range for data collection	3.69 to 19.99 º
Index ranges	–25<=h<=25, –6<=k<=6, –6<=l<=6
Reflections collected / unique	5100 / 1076 R(int) = 0.0514
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	1076 / 8 / 192
Goodness–of–fit on F^2	1.064
Final R indices [I>2sigma(I)]	R_1 = 0.0463 wR^2 = 0.1254
R indices (all data)	R_1 = 0.0468, wR^2 = 0.1265
Extinction coefficient	0.004 (2)
Largest diff. peak and hole	0.212 and –0.178 e. $Å^{-3}$

3 RESULTS AND DISCUSSION

The experimental geometry of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine presented in Figure 1 shows clearly that the vinyl group C_8=C_9 exerts changes typical for the AGIBA effect in the geometry of the pyrimidine moiety but only locally. The $C_{10}N_1$ bond length is the longest of all four CN bonds but the more distant CN bonds do not follow the pattern required by the AGIBA effect. The benzene ring, in which C=C group is *s*–trans in relation to the methoxy

group exhibit also an increased AGIBA effect since these two groups act in line in this conformation. Here the effect is observed for the whole ring. The imbalance of the Kekulé structures, calculated by use of the model HOSE [10–11] is: K_1:K_2:Q = 26.0%:48.2%:25.8%, indicating a substantial through resonance effect in the benzene part of the molecule.

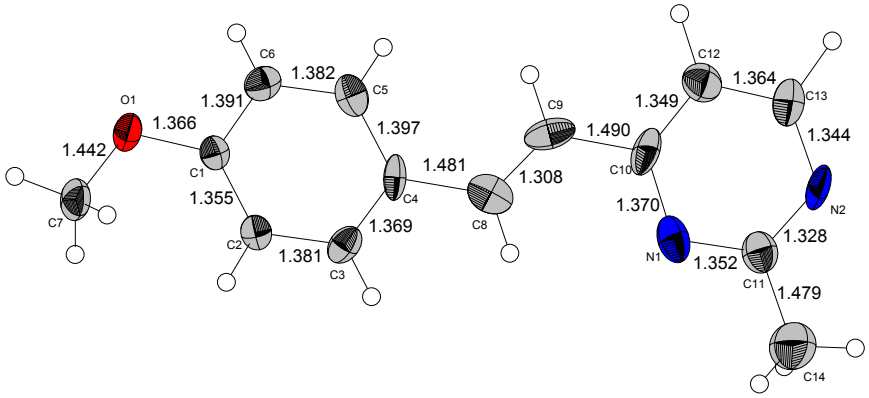
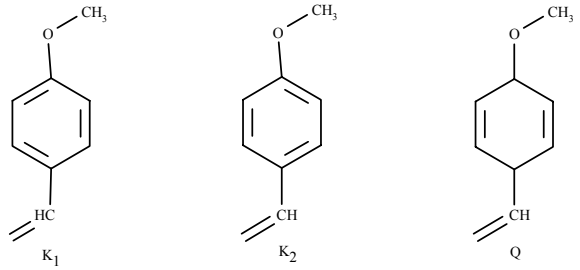


Figure 1. Bond lengths of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine with mean estimated standard deviation equal to 0.006 Å.

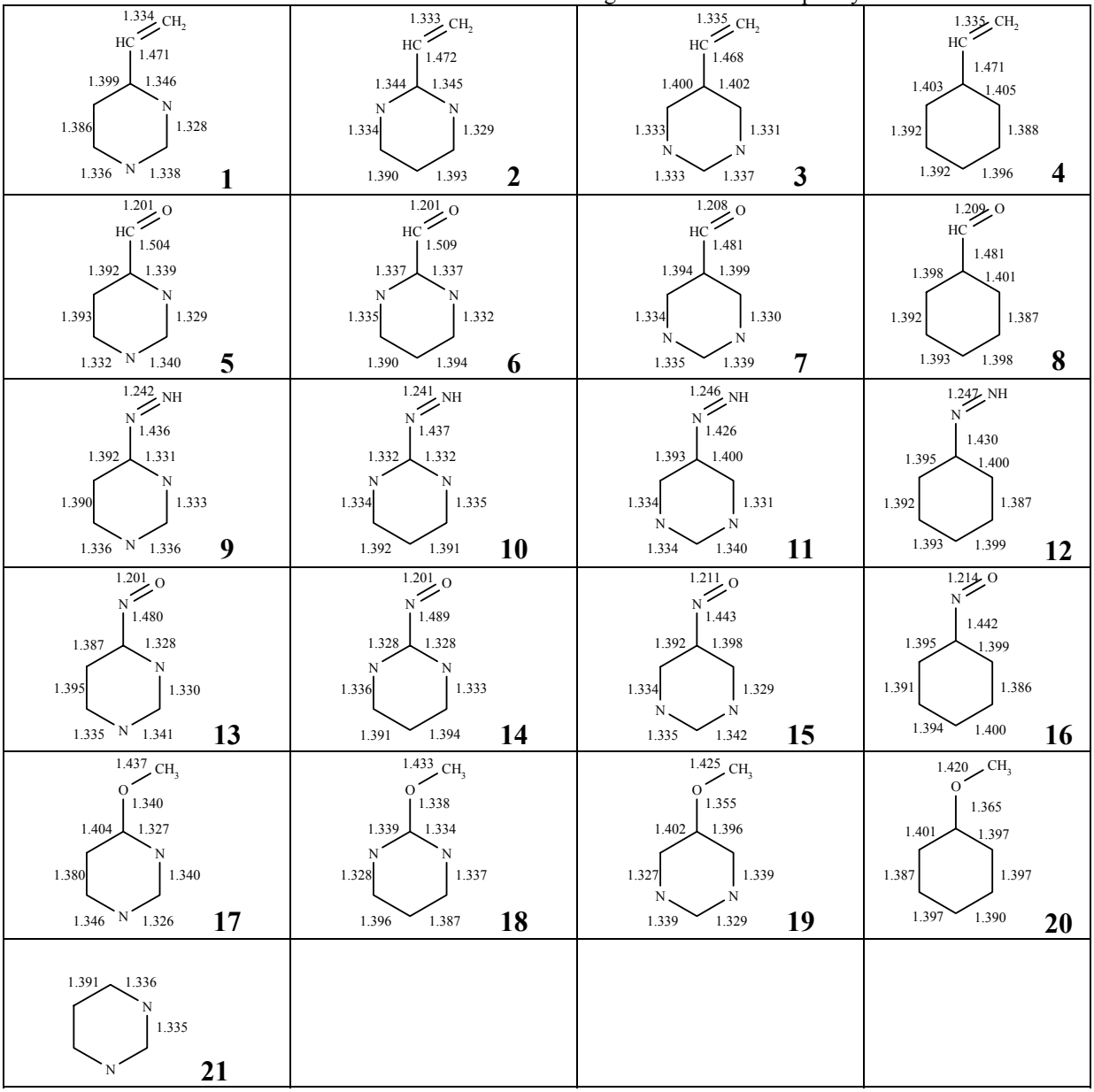
Scheme 2. Canonical structure labeling for benzene fragment of (E)–4–[2–(4–methoxyphenyl)ethenyl]–2–methylpyrimidine. In Q double bonds out of the ring not shown.



In order to get a wider and more reliable information on geometry of the various substituted pyrimidine derivatives the optimization at B3LYP/6–311G** level of theory was carried out. For comparison, the geometries of pyrimidine and its vinyl, formyl, imino, nitroso and methoxy derivatives as well as substituted in the same manner benzene derivatives are presented in Chart 1.

As it is clearly seen all CN bonds in pyrimidine (**21**) are approximately of the same length (1.335 or 1.336 Å), independently whether they are inside or outside the NCN unit. These bonds are subject of a more detailed analysis with the exclusion of molecules **9**, **10** and **14** for which the angular groups (N=NH and N=O) are out of the ring plane by the dihedral angle T > 10°. Table 2 presents geometrical data for the mentioned above molecules with the labeling as in Scheme 3.

Chart 1. The canonical structures of rings not shown for simplicity.



Scheme 3. Labeling of atoms in the ring and geometrical parameters for all systems presented in Table 2.

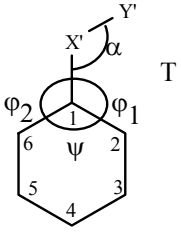
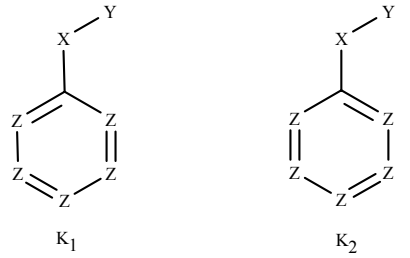


Table 2. The Kekulé structure weights (following Scheme 4) and the geometrical parameters (following Scheme 3) for the model systems of Chart 1.

	K_1[%]	K_2[%]	φ_1[°]	φ_2[°]	ψ[°]	α[°]	T[°]
1	52.8	47.2	118.6	121.1	120.3	123.9	0.0
2	51.6	48.4	118.6	116.1	125.3	124.2	0.0
3	51.5	48.5	124.8	120.4	114.7	127.8	0.0
4	52.8	47.2	117.9	118.9	123.2	127.7	0.0
5	53.9	46.1	118.4	119.4	122.0	124.7	0.0
6	51.1	48.9	118.5	114.6	126.9	124.5	0.0
7	52.2	47.8	121.8	121.8	116.4	124.1	0.0
8	53.6	46.4	120.3	119.8	119.9	124.9	0.0
9	49.4	50.6	120.2	117.0	122.7	114.0	34.2
10	49.7	50.3	118.2	113.9	127.8	113.6	47.6
11	52.6	47.4	126.1	117.0	116.9	114.4	0.0
12	54.5	45.5	124.3	115.5	120.2	114.9	0.0
13	52.1	47.9	120.8	115.5	123.7	114.3	0.0
14	50.9	49.1	119.3	112.3	128.3	113.5	11.5
15	53.2	46.8	125.4	117.1	117.5	114.8	0.0
16	54.2	45.8	123.6	115.3	121.1	115.2	0.0
17	40.6	59.4	120.1	117.8	122.1	117.6	0.0
18	46.1	53.9	119.0	113.9	127.1	117.7	0.0
19	48.5	51.5	126.5	117.2	116.4	118.1	0.0
20	44.1	55.9	124.6	115.7	119.7	118.5	0.0

Scheme 4. The canonical structures of the systems in Chart 1. X–Y represents $HC{=}CH_2$, HC=O, N=NH, N=O or $O{-}CH_3$ while Z denotes the carbon or nitrogen atom following the Chart 1.



K_1 K_2

In molecules of the series, where the angular group is attached to position as in first column of Chart 1 (molecules **1**, **5**, **9**, **13**, **17**) the bonds N_2C_3 and C_3N_4 (enumeration following the Scheme 3) became unequal by around 0.011 Å, following the requirements of the AGIBA effect. In the topologically equivalent CC bonds in the substituted benzenes (column fourth of Chart 1) this difference is only slightly smaller.

A similar picture encounters for pyrimidine derivatives substituted in position as in the third column of Chart 1. The difference between N_3C_4 and C_4N_5 bond lengths is slightly smaller, around 0.006 Å, but again following the AGIBA requirements. In the topologically equivalent CC bonds in the substituted benzenes this difference is again slightly smaller.

A quite different situation can be seen when the angular group is attached to the position as in the second column of Chart 1. Except for the methoxy derivative, the imbalance is zero. Thus it may be concluded that AGIBA effect influences pyrimidine systems when connected with methoxy group (in appropriate geometry). For the angular substituents bearing double bond the effect is less

expressed and as could be seen is limited to pyrimidine functionalized in positions 4 and 5 (colums 1 and 3 of Chart 1).

Additionally the global effect on the pyrimidine ring is studied by using the HOSE method [10–11] enabling estimation of the Kekulé structure weights, but here we are taking into account only structures K_1 and K_2 of the Scheme 2. Then three kinds of substitution are possible, exemplified by molecules in columns 1, 2 and 3 from Chart 1. In the fourth are given geometries of the benzene derivatives. Table 2 presents the imbalances of the Kekulé structures K_1 and K_2 which represent a global effect for a given ring. From these data it can be concluded that the pyrimidine moiety is less susceptible for the AGIBA effect for doubly bonded groups than the benzene ring, because the mean imbalance for columns 1, 2 and 3 are for these cases 52.9%:47.1%, 51.2%:48.8% and 52.3%:47.7% which may be compared with 53.5%:46.5% for benzene derivatives. Additionally, for the symmetrical position of the substituent (columns 2 and 3) this imbalance is the lowest. For the methoxy derivatives the imbalances in columns 2 and 3 are also the lowest, but unexpectedly the imbalance for the molecule **17**, is the highest, 40.6%:59.4%, larger than that for benzene derivative, 44.1%:55.9%. It might be interpreted by the possible interaction between the methyl group of the methoxy and the lone pair of the nitrogen.

4 CONCLUSIONS

The AGIBA effect in pyrimidine ring does work but less regularly as compared with it acting in the benzene derivatives. The double bonded groups work always weaker than in the case of benzene derivatives.

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Supplementary Material

Absolute electronic energies at B3LYP/6–311G** (in hartree) zero point vibrational energies ZPE at B3LYP/6–311G** (in kcal/mol) and Cartesian coordinates for all molecules are available.

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