Atomic Charges, Surface Electrostatic Potential Analysis, and Bond Order Analysis on Nitriles and Isocyanides

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Atomic charges, surface electrostatic potential analysis, and bond order analysis on nitriles and isocyanides

Yanyun Zhao¹, Xueli Cheng¹

Abstract

Isocyanide-nitrile rearrangement has long been a continuing and interesting topic. A series of nitriles and isocyanides with the substituents of R=-AlH₂, -BeH, -BH₂, -C≡CH, -CF₃, -CH₃, -Cl, -C≡N, -COOH, -F, -H, Li, -MgH, -Na, -NH₂, -NO₂, -OH, -PH₂, -SH, -SiH₃, -CH=CH₂ were investigated systematically based on full optimization at B3LYP-D3(BJ)/def2-QZVP level, and the isomerization energies from R-C≡N to :C=N-R were estimated. The substituent effect and bonding characters were analyzed by surface ESP colored van der Waals surfaces in conjunction with the global and local electrostatic extrema, the population analyses in terms of Hirshfeld and ADCH atomic charges, and bond order analyses via Laplacian and fuzzy bond orders.

Keywords Isocyanide-nitrile rearrangement • ESP colored van der Waals surfaces • Hirshfeld charge • ADCH charge • bond order analysis

Introduction

Organic nitriles, which have -C≡N functional groups, are a category of nitrogen-containing compounds with unique and interesting reactivity [1-4]. Their inorganic congeners are called cyanides instead. Isocyanides, also known as isonitriles or carbylamines, are isomers of nitriles and cyanides. Isocyanides were discovered as early as in 19th century but have never achieved any large-scale utility [5, 6]. However, isocyanides are also unusual and interesting due to their resonance structures and reactivity [6-8]. An isocyanide is commonly described as two resonance structures, one with an ionized triple bond between nitrogen and carbon (-N≡C) and one with a double bond (-N=C:) with a lone electron pair on carbon. In nitriles R-C≡N and isocyanides R-N=C:, the CN group can be considered as a pseudohalogen because of

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1 its high stability, strong bond strength, and large electron affinity.

2 Isocyanide-nitrile rearrangement is a continuing and charming topic. As a
3 prototypical unimolecular reaction, Gutiérrez-Oliva and coworkers [9] revisited the
4 $\text{HC}\equiv\text{N}/\text{:C}=\text{NH}$ isomerization, and concluded that this process was not a
5 straightforward proton transfer. By reason of the obvious differences between
6 $\text{CH}_3\text{NC}/\text{CH}_3\text{CN}$ and common unimolecular reactions, in 2011, Pracna *et al.* [10]
7 reported the vibrational states of CH_3NC . As early as in 1999, Sung [5] has carried out
8 a theoretical investigation on the stabilization energies and substituent effects of a set
9 of isocyanides and nitriles. However, there are no comparative studies on the bonding
10 characteristics of $\text{R}-\text{C}\equiv\text{N}$ and $\text{:C}=\text{N}-\text{R}$. In this work, a series of nitriles $\text{R}-\text{C}\equiv\text{N}$ and
11 isocyanides $\text{:C}=\text{N}-\text{R}$ ($\text{R}=-\text{AlH}_2$, $-\text{BeH}$, $-\text{BH}_2$, $-\text{C}\equiv\text{CH}$, $-\text{CF}_3$, $-\text{CH}_3$, $-\text{Cl}$, $-\text{C}\equiv\text{N}$, $-\text{COOH}$,
12 $-\text{F}$, $-\text{H}$, Li , $-\text{MgH}$, $-\text{Na}$, $-\text{NH}_2$, $-\text{NO}_2$, $-\text{OH}$, $-\text{PH}_2$, $-\text{SH}$, $-\text{SiH}_3$, $-\text{CH}=\text{CH}_2$) were chosen to
13 carry out a systematical investigation on the monomolecular isomerization of $\text{R}-\text{C}\equiv\text{N}$
14 to $\text{R}-\text{N}\equiv\text{C}$. This study will provide bond orders, surface ESP colored van der Waals
15 surfaces, Hirshfeld and ADCH atomic charges, and other fundamental physical and
16 chemical properties for these nitriles and isocyanides.

17 **Computational details**

18 The gas-phase geometries of the selected $\text{R}-\text{C}\equiv\text{N}$ and $\text{:C}=\text{N}-\text{R}$ with 21 functional
19 groups were fully optimized at B3LYP-D3(BJ)/def2-QZVP level with Gaussian 09
20 program package [11], and frequency verification was performed simultaneously to
21 confirm local minima without imaginary frequencies, and to calibrate the
22 thermodynamic parameters to 298.15 K. The traditional density functional of Becke's
23 three-parameter nonlocal exchange functional [12] with the nonlocal correlation
24 functional of Lee, Yang and Parr [13] (B3LYP) in combination with Grimme's
25 Becke-Johnson - damping D3(BJ) dispersion correction [14] is an economical and
26 highly efficient theoretical method, and can perfectly describe the possible
27 noncovalent interactions such as intramolecular hydrogen bonding and weak
28 electrovalent bonds in this work [15-19]. The quadruple zeta valence def2-QZVP
29 polarized bases proposed by Weigend and Ahlrichs [20] were employed to accurately
30 define the basis sets of these main-group elements.

In order to analyze the molecular electrostatic surfaces and bonding features, the global and local electrostatic extrema, and the molecular surface electrostatic potential (ESP) maps [21-25] were evaluated with Multiwfn 3.7 (dev) [26] and pictured by VMD 1.9.2 [27]. The ESP evaluation code based on the LIBRETA electron repulsion integral library developed by Zhang in 2018 [28] is employed in this work. Moreover, Hirshfeld population analyses [29-31] and ADCH fragment charges [32, 33] were performed using build-in sphericalized atomic densities in free states, and Laplacian bond order (LBO) [34] and fuzzy bond order (FBO) [35] analyses were carried out by means of the embedded methods in Multiwfn 3.7 (dev).

Results and discussion

The optimized geometrical parameters of the selected $R-C\equiv N$ and $:C=N-R$ in vacuum are illustrated in Fig.1. The Schönflies symbols of molecular point groups, the lowest frequencies (in cm^{-1}) and the corresponding vibrational mode assignments, and the absolute values (in a.u.) of electronic and zero-point energies E , thermal enthalpies H and thermal free energies G obtained at B3LYP-D3(BJ)/def2-QZVP level for these $R-C\equiv N$ and $:C=N-R$ are listed in Table S1 of Supplementary Materials.

Bonding strengths

The bond lengths may reflect the bonding strengths between the $-R$ groups and $-C\equiv N/-N=C:$. The nitriles $R-C\equiv N$ contain representative $-C\equiv N$ triple bonds, so they ought to be more stable than their corresponding $:C=N-R$ isomers. However, the electronegativity of N is larger than that of the C atom, so the substituents $-R$ are inclined to connect with N atoms. The bond lengths imply that the CN bonds in $:C=N-$ isocyanide groups are actually $C\equiv N-$ triple bonds. Fig. 1 also shows that, the bond distances of $R-NC$ bond is close to those of $R-C\equiv N$, and except for $R=-NH_2$, $-NO_2$ and $-OH$, the bond distances of $R-N$ are longer than those of $R-C$. Thereinto the N-N bond length (1.424 Å) of $:C=N-NO_2$ is only slightly longer than that of the N-C single bond in $O_2N-C\equiv N$. Therefore, the electron-donating and electron-accepting ability of substituents may control the stability of nitriles and isocyanides.

Fig. 1 Optimized geometrical parameters, Hirshfeld charges and isomerization energies from $R-C\equiv N$ to $:C=N-R$ at B3LYP-D3(BJ)/def2-QZVP level. Numerical values in pink beside atoms are atomic Hirshfeld charges. Bond lengths are in Å, and isomerization energies are in kcal/mol

The isomerization energies from $R-C\equiv N$ to $:C=N-R$ are also shown in Fig. 1, where the nitriles $R-C\equiv N$ ($R=-AlH_2$, $-BeH$, $-Li$, $-MgH$ and $-Na$) are less stable than their $:C=N-R$ isomers by 2.8, 5.7, 3.7, 2.6 and 1.6 kcal/mol, respectively. The tiny energy discrepancies between these highly ionic isomer pairs may denote that the cations will not lie arbitrarily on single C or N atoms. The triangular configurations of $R = -Na$ and $-Li$ were located at B3LYP-D3(BJ)/def2-QZVP level in vacuum, and this theoretical model confirmed that these two triangular geometries are more stable than their cyanide isomers ($Na-C\equiv N$ and $Li-C\equiv N$) in energy. The relative free energy of the triangle $Na-C\equiv N$ is even lower than that of $:C=N-R$ by 1.6 kcal/mol, as illustrated in Fig. S1 of Supplementary Materials. The largest energy discrepancy appears in $F-C\equiv N$, which is more stable than $:C=N-F$ by 68.0 kcal/mol. The isomerization energies accord excellently with the stabilization energies correlated with Taft's dual-substituent parameters [5, 36].

Atomic charges and population analyses

Hirshfeld charges are qualitatively consistent with general chemical concepts, and can quantify electrophilicity and nucleophilicity of molecular surfaces [37, 38], so Hirshfeld charges and Hirshfeld fragment charges will reflect the amount of transferred electron density, and can materialize the electron-donating and electron-accepting ability of substituents. However, Lu and Chen [32] put forward that atomic dipole moments were completely neglected in Hirshfeld charges, and proposed the Atomic Dipole Moment Corrected Hirshfeld (ADCH) atomic charges. The normalized Hirshfeld charges are shown in Fig. 1, and fragmental Hirshfeld $q_R(\text{Hirshfeld})$ and ADCH charges $q_R(\text{ADCH})$ between the substituents $-R$ and $-C\equiv N/-N=C:$ are listed in Table 1. The fragment charges are also normalized to actual numbers of electrons.

Fig. 2 Molecular surface electrostatic potential maps at 0.001 e/bohr³. Positive and negative surface potentials are revealed as red and blue regions. The values near ESP surface extreme points are global and local electrostatic extrema (in kcal/mol)

Table 1 The fragment Hirshfeld q_R (Hirshfeld) and ADCH charges q_R (ADCH), the LBO and FBO indices (I_{LBO} and I_{FBO}) involving the bonds of R-C($\equiv$ N)/(:C=N)-R and the corresponding fragment indices ($I_{LBO}^{Seg.}$ and $I_{FBO}^{Seg.}$) between the two segments. ΔI_{FBO} is the difference between $I_{FBO}^{Seg.}$ and I_{FBO} . The two fragments are defined as the -R group and the -C $\equiv$ N/:C=N- group

	Species	q_R (Hirshfeld)	q_R (ADCH)	I_{LBO}	$I_{LBO}^{Seg.}$	I_{FBO}	$I_{FBO}^{Seg.}$	ΔI_{FBO}
R-C $\equiv$ N	R=-AlH ₂	0.295	0.304	0.753	0.753	1.017	1.292	0.275
	R=-BeH	0.272	0.269	0.666	0.666	0.910	1.098	0.188
	R=-BH ₂	0.152	0.179	1.223	1.223	1.126	1.459	0.333
	R=-C $\equiv$ CH	0.083	0.076	1.642	1.642	1.319	1.792	0.473
	R=-CF ₃	0.074	0.114	1.303	1.303	0.965	1.486	0.521
	R=-CH ₃	0.157	0.211	1.246	1.247	1.239	1.614	0.375
	R=-Cl	0.118	0.183	1.067	1.067	1.453	1.765	0.312
	R=-C $\equiv$ N	0.000	0.000	1.618	1.618	1.269	1.704	0.435
	R=-COOH	0.070	0.145	1.311	1.311	1.040	1.533	0.493
	R=-F	0.019	0.074	0.341	0.341	1.472	1.698	0.226
	R=-H	0.126	0.282	0.963	0.963	0.899	0.970	0.071
	R=-Li	0.584	0.796	0.140	0.140	0.670	0.785	0.115
	R=-MgH	0.422	0.397	0.456	0.456	0.926	1.131	0.205
	R=-Na	0.618	0.801	0.214	0.214	0.799	0.949	0.150
	R=-NH ₂	0.165	0.227	1.269	1.269	1.480	1.842	0.362
	R=-NO ₂	-0.011	0.023	1.008	1.008	1.051	1.629	0.578
	R=-OH	0.108	0.230	0.815	0.815	1.521	1.823	0.302
	R=-PH ₂	0.203	0.204	1.113	1.113	1.265	1.630	0.365
	R=-SH	0.173	0.213	1.191	1.191	1.417	1.773	0.356
	R=-SiH ₃	0.219	0.248	1.039	1.039	1.103	1.434	0.331
	R=-CH=CH ₂	0.144	0.176	1.393	1.393	1.223	1.697	0.474
:C=N-R	R=-AlH ₂	0.306	0.310	0.403	0.403	1.121	1.391	0.270
	R=-BeH	0.273	0.263	0.316	0.316	0.989	1.179	0.190
	R=-BH ₂	0.147	0.169	0.792	0.792	1.227	1.560	0.333
	R=-C $\equiv$ CH	0.070	0.053	1.345	1.345	1.406	1.905	0.499
	R=-CF ₃	0.090	0.125	1.027	1.027	1.051	1.620	0.569
	R=-CH ₃	0.184	0.229	0.823	0.823	1.244	1.620	0.376
	R=-Cl	0.127	0.172	0.713	0.713	1.523	1.847	0.324
	R=-C $\equiv$ N	-0.007	-0.019	1.365	1.365	1.388	1.850	0.462
	R=-COOH	0.082	0.161	1.000	1.000	1.125	1.654	0.529
	R=-F	0.033	0.070	0.259	0.259	1.469	1.713	0.244
	R=-H	0.184	0.351	0.803	0.803	0.862	0.947	0.085
	R=-Li	0.598	0.825	0.071	0.071	0.669	0.790	0.121
	R-MgH	0.447	0.416	0.248	0.248	0.980	1.182	0.202
	R=-Na	0.651	0.843	0.122	0.122	0.782	0.938	0.156
	R=-NH ₂	0.175	0.236	0.845	0.845	1.433	1.806	0.373
	R=-NO ₂	0.045	0.067	0.597	0.597	1.074	1.701	0.627

R=-OH	0.121	0.232	0.544	0.544	1.489	1.802	0.313
R=-PH ₂	0.213	0.209	0.683	0.683	1.348	1.718	0.370
R=-SH	0.182	0.229	0.778	0.778	1.482	1.847	0.365
R=-SiH ₃	0.228	0.251	0.598	0.598	1.213	1.547	0.334
R=-CH=CH ₂	0.150	0.178	1.001	1.001	1.260	1.749	0.489

The Hirshfeld charges in Fig. 1 shows that, in nitriles and isocyanides, except for R=-COOH and R=-NO₂, the N atoms of -C≡N and :C=N- groups are the negative charge centers. In :C=N-CF₃, the negative center is the F atoms other than the N atom. The Hirshfeld charges reveal electron distribution in R-C≡N and :C=N-R.

The fragment Hirshfeld charges (Table 1) demonstrate that the electron-donating ability of -R is -Na (0.618) > -Li (0.584) > -MgH (0.422) > -AlH₂ (0.295) > -BeH (0.272) > -SiH₃ (0.219) > -PH₂ (0.203) > -SH (0.173) > -NH₂ (0.165) > -CH₃ (0.157) > -BH₂ (0.152) > -CH=CH₂ (0.144) > -H (0.126) > -Cl (0.118) > -OH (0.108) > -C≡CH (0.083) > -CF₃ (0.074) > -COOH (0.070) > -F (0.019) > -C≡N (0.000) > -NO₂ (-0.011) for R-C≡N, and -Na (0.651) > -Li (0.598) > -MgH (0.447) > -AlH₂ (0.306) > -BeH (0.273) > -SiH₃ (0.228) > -PH₂ (0.213) > -CH₃ (0.184) ≈ -H (0.184) > -SH (0.182) > -NH₂ (0.175) > -CH=CH₂ (0.150) > -BH₂ (0.147) > -Cl (0.127) > -OH (0.121) > -CF₃ (0.090) > -COOH (0.082) > -C≡CH (0.070) > -F (0.033) > -NO₂ (0.045) > -C≡N (-0.007) for :C=N-R. These electron-donating orders confirm that functional groups (e.g. -C≡N and :C=N- in the present work) will slightly influence charge distribution. For example, the -NO₂ group is an electron-accepting group in nitriles/cyanides but an electron-donating one in isocyanides, and the -C≡N group is the only electron-donating group for isocyanides.

In general, the ADCH fragment charges predict similar orders for the electron-donating capability of nitriles and isocyanides except for some substituents. Both the Hirshfeld and ADCH charges approve an electron-attracting property of -C≡N in :C=N-C≡N. The values of ADCH fragment charges for typical cations such as -Na (0.801 e for Na-C≡N and 0.843 e for :C=N-Na) and -Li (0.796 e for Li-C≡N and 0.825 e for :C=N-Li) agree better with our chemical intuition, and are much larger than the corresponding Hirshfeld charges. The ADCH fragment charge of -H (0.351 e) indicates that the H atom in :C=N-H is highly ionic. On the whole, the electron

1 interactions between the substituents and $\text{-C}\equiv\text{N}/\text{:C}=\text{N-}$ impose important influence on
2 the charge distribution.

3 The molecular surface ESP colored van der Waals surface maps of $\text{R-C}\equiv\text{N}$
4 and $\text{:C}=\text{N-R}$, and the global and local electrostatic extrema calculated from
5 quantitative analyses of molecular surfaces are shown in Fig. 2. The ESP maps of
6 $\text{R-C}\equiv\text{N}$ and $\text{:C}=\text{N-R}$ visually display electron distribution on molecular surfaces.
7 From Fig. 2 it can be seen that the N atoms in both $\text{-C}\equiv\text{N}$ and $\text{:C}=\text{N-}$ are always the
8 ESP negative centers, and the surfaces potentials properly reveal the acidity of H
9 atoms. However, for the triangular $\text{:C}=\text{N-Na}$ and $\text{:C}=\text{N-Li}$ (Fig. S1), the negative
10 charge centers are the C atoms instead of the N atoms. When H atoms are bonded to
11 nonmetallic elements, the electrostatic extrema of these H atoms are apparently
12 positive. The high potential extrema of the H atoms in $\text{HOOC-C}\equiv\text{N}$ (67.69 kcal/mol)
13 and $\text{:C}=\text{N-COOH}$ (67.33 kcal/mol) confirm the high acidity of carboxyl H atoms. The
14 H atoms in $\text{H-C}\equiv\text{N}$ (52.03 kcal/mol) and $\text{:C}=\text{N-H}$ (67.05 kcal/mol) also possess high
15 positive extrema, according well with the results of the Hirshfeld and ADCH fragment
16 charges. The H atoms linking to metal atoms, just as in the substituents of -BeH and
17 -MeH , are of negative ESP extrema. The extrema of H atoms in $\text{H}_2\text{Al-C}\equiv\text{N}$
18 and $\text{:C}=\text{N-AlH}_2$ are 0.89 and -0.29 kcal/mol, suggesting that the Al-H bonds in
19 $\text{H}_2\text{Al-C}\equiv\text{N}$ involving amphoteric element Al represent apparent covalency. The
20 positive ESP extrema near Na and Li atoms are very large, proving that they are in the
21 form of ionic Na^+ and Li^+ . The ESP extremum of Li^+ in $\text{:C}=\text{N-Li}$ is even undetectable
22 by Multiwfn 3.7 (dev).

23 **Bond order analyses**

24 Bond order analysis is a numerical description of the number of electrons and bond
25 strength involved in bonds between two atoms or molecular segments. The fuzzy
26 bond order (FBO) is commonly employed as an indicator of the stability of a chemical
27 bond [39-41]. FBO is the delocalization index calculated in fuzzy atomic space, and is
28 the most popular and adaptive bond order index [42-44]. The Laplacian bond orders
29 (LBO) index is defined a covalent bond order based on the Laplacian of electron
30 density in fuzzy overlap space, so it may be unsuitable for highly ionic species.

However, LBO has been proved to be an excellent bond order index to a wide variety of molecules [34, 45], so Laplacian bond orders for ionic compounds are still listed in Table 1. The LBO and FBO indices (I_{LBO} and I_{FBO}) involving the bonds between substituents -R and -C $\equiv$ N/:C=N-, and between the two segments ($I_{\text{LBO}}^{\text{Seg.}}$ and $I_{\text{FBO}}^{\text{Seg.}}$) of the -R group and the -C $\equiv$ N/:C=N- group are also listed in Table 1.

The Laplacian bond orders are in a direct correlation with the bond polarity, so the LBO indices of fragments almost equal to those of the bonds, as validated by the bond orders in Table 1. Moreover, the Laplacian bond orders of R-C $\equiv$ N are clearly larger than those of their :C=N- isomers. Nevertheless, apart from R= -Li, -Na, -F, -H and -NH₂, the I_{FBO} values of isocyanides are larger than their nitrile isomers. While for $I_{\text{FBO}}^{\text{Seg.}}$, only the values of :C=N-R (R= -Na, -H, -NH₂ and -OH) are less than those of their R-C $\equiv$ N counterparts.

The fragment FBO values are obviously larger than those of the corresponding R-C($\equiv$ N)/(:C=N)-R bonds, which testifies evident electron-delocalizing effect between -R and the -C $\equiv$ N/:C=N- group. The difference values between $I_{\text{FBO}}^{\text{Seg.}}$ and I_{FBO} are assigned as ΔI_{FBO} , and are also shown in Table 1. The large ΔI_{FBO} of R = -NO₂, -CF₃, -COOH, -CH=CH₂, -C $\equiv$ CH and -C $\equiv$ N may denote strong overlaps between the two fragments. In general, the ΔI_{FBO} values show that the two fragments overlap more in :C=N-R than in their isomers R-C $\equiv$ N except for some isomeric pairs such as HMg-C $\equiv$ N and :C=N-MgH.

Conclusion

In the present work, 21 isomer pairs of nitriles R-C $\equiv$ N and isocyanides :C=N-R (R=-AlH₂, -BeH, -BH₂, -C $\equiv$ CH, -CF₃, -CH₃, -Cl, -C $\equiv$ N, -COOH, -F, -H, Li, -MgH, -Na, -NH₂, -NO₂, -OH, -PH₂, -SH, -SiH₃, -CH=CH₂) were fully optimized at B3LYP-D3(BJ)/def2-QZVP level. The isomerization energies from R-C $\equiv$ N to :C=N-R, and the atomic charges were calculated. Whereafter, population analyses and bond order analyses were carried out. The Hirshfeld charges were analyzed to reveal electron distribution in R-C $\equiv$ N and :C=N-R. The isomerization energies show that the

1 isocyanides of R-C≡N (R=-AlH₂, -BeH, -Li, -MgH and -Na) are more stable than
2 their nitrile isomers by 2.8, 5.7, 3.7, 2.6 and 1.6 kcal/mol, respectively. The fragment
3 Hirshfeld charges and ADCH fragment charges demonstrate the sequences of
4 electron-donating ability for isocyanides and nitriles. The ADCH fragment charge
5 of :C=N-H indicates that the H atom is also highly ionic. The surface ESP maps
6 visually reveal electron distribution on molecular surfaces, and the surface
7 electrostatic extrema can also reflect electron distribution quantitatively. The LBO
8 indices of fragments almost equal to those of the bonds, implying that LBO indices
9 have already considered electron delocalization and fragment effects. In this work, the
10 difference values ΔI_{FBO} between the fuzzy bond orders of the fragments and the bonds
11 elucidate electron delocalization and overlaps of electron density between the two
12 fragments.

13
14 **Supplementary Information** The online version contains supplementary
15 material available at <https://doi.org/10.1007/>

16
17 **Author's contributions** Yanyun Zhao: Software, Formal analysis, Investigation,
18 Writing - original draft; Xueli Cheng: Conceptualization, Methodology, Software,
19 Writing - original draft and editing; Management and responsibility for the research
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25
26 **Data availability** All data generated or analyzed during this study are included in this
27 published article.

28
29 **Compliance with ethical standards**

Conflicts of Interest The authors declare that they have no competing interests.

Consent for publication Written informed consent for publication was obtained from all participants.

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Figures

Figure 1

Optimized geometrical parameters, Hirshfeld charges and isomerization energies from $R-C\equiv N$ to $:C=N-R$ at B3LYP-D3(BJ)/def2-QZVP level. Numerical values in pink beside atoms are atomic Hirshfeld charges. Bond lengths are in Å, and isomerization energies are in kcal/mol

Figure 2

Molecular surface electrostatic potential maps at 0.001 e/bohr³. Positive and negative surface potentials are revealed as red and blue regions. The values near ESP surface extreme points are global and local electrostatic extrema (in kcal/mol)

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