

Benzene-Based Carboxylic Acids: A DFT Study of the Effect of Alkyl-Chain Length on Structural, Thermochemical and Electronic Properties

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ABSTRACT

A systematic density functional theory (DFT) investigation was performed to examine the influence of alkyl-chain length on the structural, energetic, thermochemical, and electronic properties of **benzene-based alkyl carboxylic acids**. A homologous series of 4-alkylbenzoic acids, ranging from 4-methylbenzoic acid to 4-sexylbenzoic acid, was studied at the B3LYP/6-311G(d,p) level using Gaussian 09. The optimized molecular structures were analyzed in terms of total electronic energy, dipole moment, thermal energy, heat capacity, and entropy. The results reveal a systematic variation in molecular properties with increasing alkyl-chain length. The total electronic energy becomes progressively more negative, while the dipole moment shows an overall increasing tendency. The thermochemical parameters, including thermal energy, heat capacity and entropy, increase consistently with chain extension, indicating enhanced molecular complexity and conformational flexibility. Frontier molecular orbital analysis shows a gradual reduction in the HOMO-LUMO energy gap from **5.6159 to 5.5824 eV**, accompanied by systematic changes in the global reactivity descriptors. These results demonstrate that progressive alkyl-chain extension produces measurable changes in the stability, thermochemical behavior and electronic reactivity of benzene-based alkyl carboxylic acids. The study provides useful theoretical insights into the structure–property relationship of this class of substituted aromatic carboxylic acids.

Keywords: DFT; B3LYP; HOMO-LUMO; Alkyl chain; Thermochemistry; Reactivity.

INTRODUCTION

Benzoic acid and its derivatives constitute an important class of aromatic carboxylic acids because their physicochemical and electronic properties can be systematically modulated through substitution on the aromatic ring. Benzoic acid and its derivatives have found applications in food preservation, pharmaceutical formulations, chemical synthesis, cosmetics and other industrial processes, owing to their antimicrobial properties and versatile chemical reactivity [1-3]. The introduction of different substituents into the benzene ring can significantly alter the electronic structure, acidity, molecular stability and reactivity of the parent benzoic acid framework. In particular, systematic investigations of substituent effects provide useful insights into structure property relationships and the factors governing the behavior of substituted aromatic carboxylic acids.

The electronic effects of substituents in benzoic acid derivatives have been extensively investigated using both experimental and theoretical approaches. Hollingsworth *et al.* demonstrated that substituent-induced changes in the electronic structure of benzoic acids can be effectively examined using density functional theory (DFT), with calculated electronic descriptors showing meaningful relationships with experimentally observed acidity trends [4]. More recently, energetic characteristics of substituted benzoic acids have also been examined in terms of total molecular energies, emphasizing the usefulness of quantum-chemical calculations for understanding

substituent effects in these systems [5]. These studies indicate that even apparently simple structural modifications can produce measurable changes in molecular energetics and electronic properties.

Density functional theory has become a powerful computational approach for investigating molecular structures, energetics and chemical reactivity. Hybrid functionals such as B3LYP combine exchange and correlation contributions and have been widely employed for the study of organic molecular systems [6-8]. The conceptual DFT framework further provides global descriptors such as electronegativity, chemical potential, hardness, softness and electrophilicity, which can be derived from frontier molecular orbital properties and used to characterize the chemical behavior of molecular systems [9,10]. In particular, the HOMO-LUMO energy separation is commonly employed as an electronic descriptor associated with molecular stability and reactivity, while the electrophilicity index provides a quantitative measure of the tendency of a molecular system to accept electronic charge.

Despite extensive studies of substituted benzoic acids, a systematic computational assessment of the effect of **progressively increasing para-alkyl-chain length** on the structural, energetic, thermochemical and global reactivity characteristics of 4-alkylbenzoic acids remains of interest. In the present work, a homologous series of 4-alkyl-substituted benzoic acids, ranging from **4-methylbenzoic acid to 4-sexylbenzoic acid**, is investigated using DFT. The study examines the influence of alkyl-chain length on molecular energy, dipole moment, thermochemical parameters, frontier molecular orbitals and global reactivity descriptors. The calculated trends provide a systematic picture of how incremental alkyl-chain extension influences the stability, flexibility and electronic reactivity of the benzoic-acid framework, thereby contributing to a better understanding of structure property relationships in para-alkyl-substituted aromatic carboxylic acids. The selected series and calculated properties are consistent with the subsequent results presented in the uploaded manuscript.

METHODOLOGY

The molecular structures of the investigated 4-alkyl-substituted benzoic acids were optimized using **Density Functional Theory (DFT)** employing the **B3LYP hybrid exchange-correlation functional** with the **6-311G(d,p) basis set** [11-14]. All calculations were performed using the **Gaussian 09** software package [15]. Complete geometry optimization was carried out without geometrical constraints, followed by vibrational frequency calculations at the same theoretical level to confirm the nature of the optimized structures. The absence of imaginary frequencies was taken as evidence that the optimized geometries correspond to minima on the potential-energy surface. The optimized structures were subsequently used to obtain total electronic energies, dipole moments, thermal energies, constant-volume heat capacities (C_v), and entropies (S). The systematic variation of these properties with alkyl-chain length was used to investigate the structural and thermochemical effects associated with progressive chain extension. The optimized molecular geometries were visualized using **GaussView 5.0** [16].

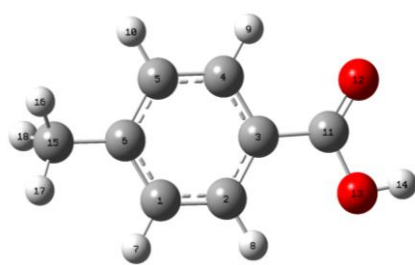
The electronic properties were further investigated through **frontier molecular orbital (FMO) analysis**, using the calculated HOMO and LUMO energies. The HOMO-LUMO energy gap was obtained from $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$. Global reactivity descriptors, including ionization potential (IP), electron affinity (EA), electronegativity (χ), chemical potential (μ), chemical hardness (η), softness (S), and electrophilicity index (ω), were evaluated from the frontier orbital energies following the conceptual DFT formalism. The electrophilicity index was calculated according to Parr *et al.* [9]. The spatial distributions of the HOMO and LUMO were examined using GaussView 5.0 to assess the localization of frontier electron density and identify changes associated with increasing alkyl-chain length.

RESULTS AND DISCUSSION

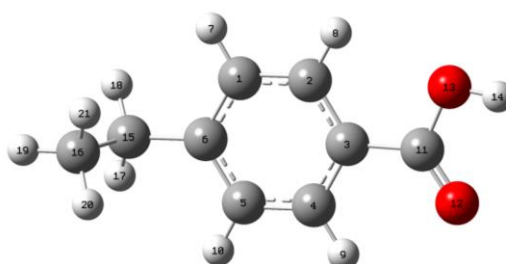
3.1. Energetic and Dipole Moment Analysis

The calculated energies of 4-alkyl substituted benzoic acids exhibit a systematic trend where molecular stability increases with the length of the alkyl chain. As shown in Table 1, the total electronic energy becomes progressively more negative from 4-methylbenzoic acid (-460.2679 Hartree) to 4-sexylbenzoic acid (-656.8890

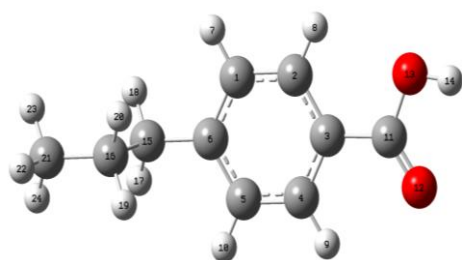
Hartree). This is indicative of enhanced stability attributed to the increasing size and electron count of the alkyl substituent.



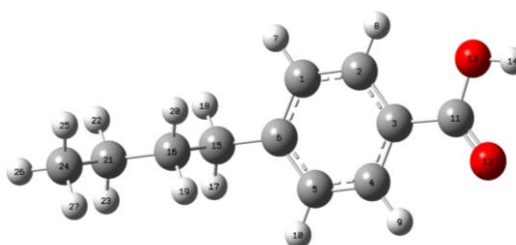
(a) 4-methylbenzoic acid



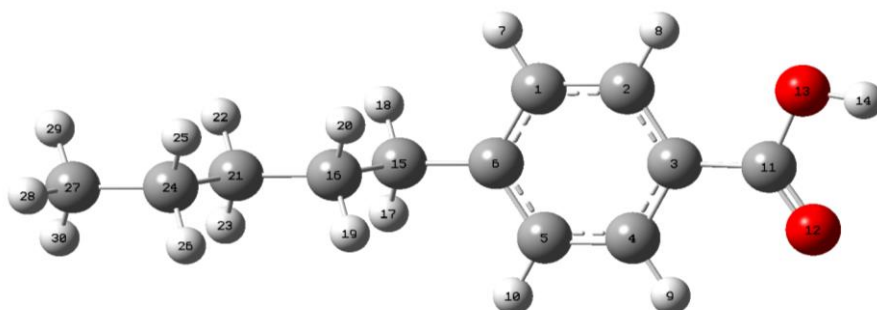
(b) 4-ethylbenzoic acid



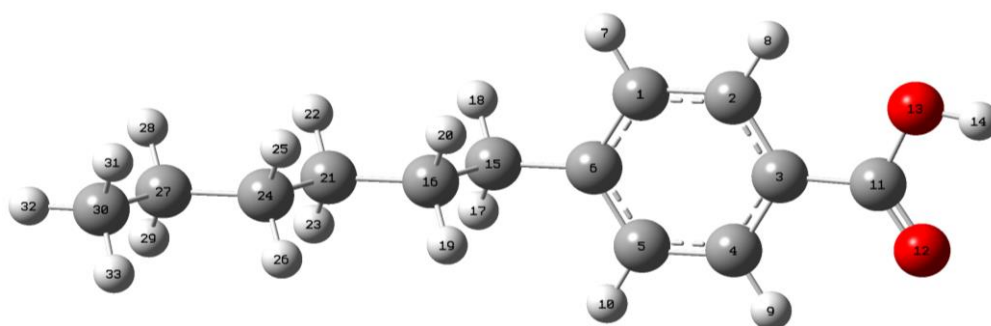
(c) 4-propylbenzoic acid



(d) 4-butylbenzoic acid



(e) 4-pentylbenzoic acid



(f) 4-hexylbenzoic acid

Fig 1 Illustrates the optimized geometries of the 4-alkyl ($n = 1-6$) benzoic acids, reflecting the spatial elongation of the molecule as the alkyl chain lengthens.

Table 1: Energy and Dipole moment of 4-alkyl (n=1-6) benzoic acid.

Molecule	Energy (Hartree)	Dipole moment (Debye)
4-methylbenzoic acid	-460.2679	2.3573
4-ethylbenzoic acid	-499.5919	2.3658
4-propylbenzoic acid	-538.9164	2.4045
4-butylbenzoic acid	-578.2406	2.4680
4-pentylbenzoic acid	-617.5648	2.4608
4-sexylbenzoic acid	-656.8890	2.5053

In terms of dipole moments, a modest increasing trend is observed. The dipole moment rises from 2.3573 Debye for 4-methylbenzoic acid to 2.5053 Debye for 4-sexylbenzoic acid, suggesting a nearly linear relationship between chain length and dipole moment, although minor fluctuations exist.

Thermochemical Properties

A consistent increase in thermodynamic properties is observed with increasing alkyl chain length. As shown in Table 2, the thermal energy (E_{thermal}) increases significantly from 95.106 kcal/mol for the methyl derivative to 188.43 kcal/mol for the sexyl derivative. This increase can be attributed to the greater number of vibrational and rotational modes introduced by longer alkyl chains.

Likewise, heat capacity (C_v) and entropy (S) also show an upward trend. C_v increases from 33.365 to 57.576 Cal/mol-K, and entropy rises from 94.639 to 130.614 Cal/mol-K, indicating higher molecular flexibility and complexity with larger alkyl groups.

Table 2: Thermochemistry of 4-alkyl (n=1-6) benzoic acid.

Molecule	E_{thermal} (kcal/mol)	C_v (Cal/Mol-kelvin)	S (Cal/Mol-kelvin)
4_methylbenzoic acid	95.106	33.365	94.639
4_ethylbenzoic acid	113.889	38.074	100.312
4_propylbenzoic acid	132.521	42.959	107.778
4_butylbenzoic acid	151.152	47.841	115.37
4_pentylbenzoic acid	169.804	52.692	122.953
4_sexylbenzoic acid	188.43	57.576	130.614

Similarly, the heat capacity at constant volume (C_v) and entropy (S) both increase across the series. C_v ranges from 33.365 to 57.576 Cal/Mol-K, while entropy increases from 94.639 to 130.614 Cal/Mol-K. These trends are consistent with increased molecular complexity and conformational flexibility as the alkyl chain lengthens.

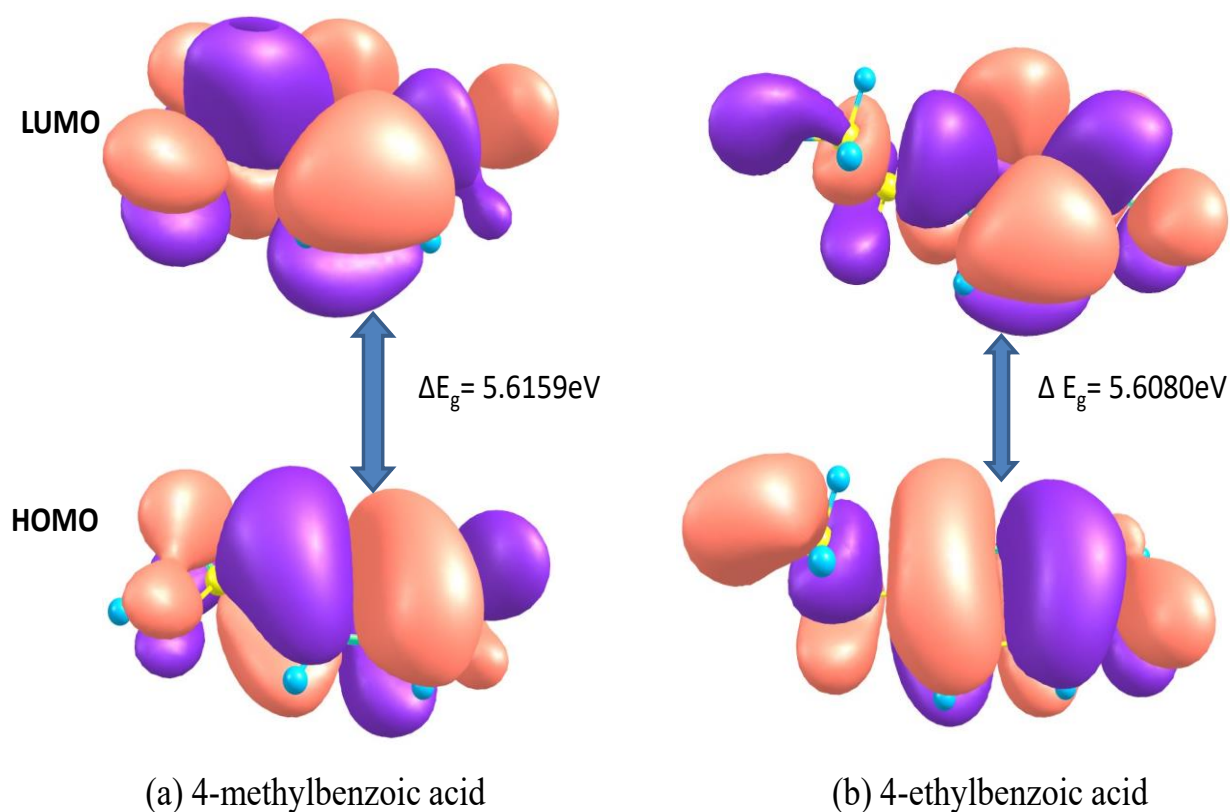
Global Reactivity Parameters

The frontier molecular orbital (FMO) analysis reveals subtle changes in electronic properties as the alkyl chain length increases. The HOMO energies gradually become less negative (from -7.0642 eV to -7.0185 eV), indicating a slight increase in electron-donating ability. Meanwhile, the LUMO energies show minimal variation,

resulting in a small but consistent decrease in the HOMO-LUMO energy gap from 5.6159 eV to 5.5824 eV (Table3), which suggests a marginal increase in chemical reactivity.

Table 3: Global reactivity parameters of 4-alkyl (n=1-6) benzoic acid.

Global reactivity parameters	4_methylbenzoic acid	4_ethylbenzoic acid	4_propylbenzoic acid	4_butylbenzoic acid	4_pentylbenzoic acid	4_hexylbenzoic acid
HOMO (eV)	-7.0642	-7.0667	-7.0414	-7.0277	-7.0226	-7.0185
LUMO (eV)	-1.4483	-1.4587	-1.4475	-1.4404	-1.4380	-1.4361
IP (eV)	7.0642	7.0667	7.0414	7.0277	7.0226	7.0185
EA (eV)	1.4483	1.4587	1.4475	1.4404	1.4380	1.4361
Electronegativity (eV)	4.2563	4.2627	4.2444	4.2341	4.2303	4.2273
Chemical potential (eV)	-4.2563	-4.2627	-4.2444	-4.2341	-4.2303	-4.2273
Hardness (eV)	-2.8079	-2.8040	-2.7969	-2.7937	-2.7923	-2.7912
Softness (eV ⁻¹)	-0.3561	-0.3566	-0.3575	-0.3580	-0.3581	-0.3583
Electrophilicity index (eV)	-3.2258	-3.2401	-3.2205	-3.2086	-3.2044	-3.2011
Energy gap (eV)	5.6159	5.6080	5.5938	5.5873	5.5846	5.5824



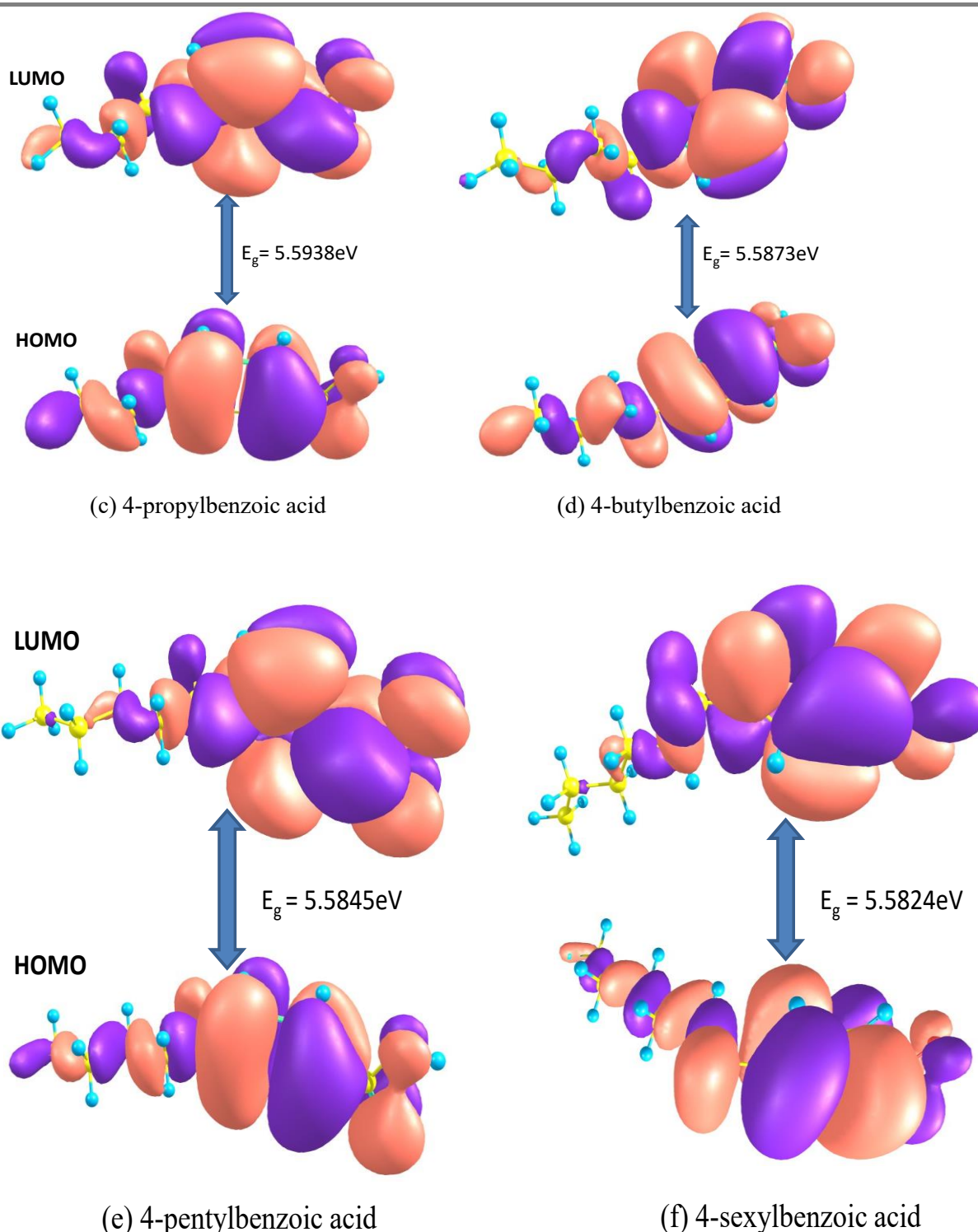


Fig 2 Presents the frontier molecular orbitals of these molecules, which illustrate the distribution of electron densities and the localization of reactive sites.

Electronegativity and chemical potential both decrease slightly across the series, suggesting that longer alkyl chains make the molecules slightly more nucleophilic. Similarly, hardness values become marginally less negative, and softness increases slightly, reinforcing the notion of increasing reactivity. The electrophilicity index also follows a decreasing trend (from -3.2258 eV to -3.2011 eV), suggesting that these molecules become marginally less electrophilic as the alkyl chain grows.

CONCLUSION

All computational calculations in this study were performed using Density Functional Theory (DFT). The B3LYP hybrid functional combined with the 6-311G basis set was utilized for geometry optimization and frequency calculations of 4-alkyl substituted benzoic acids (alkyl chain length: methyl to sexyl). Optimized molecular geometries were confirmed as minima on the potential energy surface through frequency analysis, ensuring the absence of imaginary frequencies. Frontier molecular orbital (FMO) energies and global reactivity descriptors, including electronegativity, chemical potential, hardness, softness, and electrophilicity indices, were determined from the computed HOMO and LUMO energies.

The computational study provided insights into the structural, thermochemical, and electronic properties of para-substituted 4-alkylbenzoic acids. Results indicated enhanced molecular stability with increasing alkyl chain length, as reflected by decreasing total energies. The thermochemical parameters, such as thermal energy, entropy, and heat capacity, exhibited consistent increments corresponding to greater molecular flexibility and complexity of larger alkyl substituents. Furthermore, global reactivity descriptors demonstrated a subtle decrease in energy gaps and hardness values with longer alkyl groups, indicating marginally increased nucleophilicity and reactivity. Overall, the theoretical analysis establishes foundational data beneficial for designing alkyl-substituted benzoic acids for specific applications.

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