ABSTRACT: Two stacking manners, that is, \( \pi \)- and lamellar stacking, are generally found for organic semiconductors, in which the \( \pi \)-stacking occurs between conjugated groups and the lamellar stacking refers to the separation of the conjugated and aliphatic moieties. The stacking principles are yet not well-defined. In this work, extended transition state–natural orbitals for chemical valence (ETS–NOCV), an energy decomposition analysis, is utilized to examine the \( \pi \)- and lamellar stacking for a series of naphthalenetetracarboxylic diimide (R-NDI) crystals. The crucial role of dispersion is validated. The perception that \( \pi \)-stacking is merely determined by the conjugated moiety is challenged. The stacking principles are associated with the closest packing model. Nanoscopic phase separation of conjugated and aliphatic moieties and the formation of lamellar and herringbone motifs in the R-NDIs can thus be clarified. Moreover, the interactions between NDI and the alkyl chain are investigated, revealing that the interactions can be significant, being contradictory to the conventional point of view. Along with R-NDIs, additional organic crystals consisting of various conjugated functionalities and substituents are also investigated by ETS–NOCV. The sampling scope is up to 108 conjugated molecules. The dominant role of dispersion force irrespective of the variation in the conjugated moieties and substituents is further confirmed. It is envisaged that the established principles are applicable to other organic semiconductors. The perspective toward the \( \pi \)- and lamellar stacking might be modified, paving the way for ultimate morphological control.

INTRODUCTION

Organic semiconductors have been used extensively in organic photovoltaics,\(^1,2\) organic field-effect transistors,\(^3\)–\(^5\) organic light-emitting diodes,\(^6\)–\(^8\) organic biomedical devices,\(^9,10\) and so on. The device performance is associated with numerous factors, such as chemical functionality,\(^11\) chemical structure,\(^12,13\) molecular weight,\(^14,15\) morphology,\(^16\) and device architecture.\(^17,18\) Among all, the effect of morphology is often prominent. The morphology can be quantified by the parameter of order. One extreme is amorphous, and the other is crystalline. It is common for organic semiconductors to have both amorphous and crystalline regions, especially in solution-processed organic thin films. Two stacking manners, that is, \( \pi \)- and lamellar stacking, are generally found for the order domains, in which the \( \pi \)-stacking occurs between conjugated groups and the lamellar stacking usually refers to the regular separation of the conjugated and aliphatic moieties (Scheme 1).\(^19\) Moreover, two packing motifs lamella (Scheme 1a) and herringbone (Scheme 1b) are typically utilized to describe the relationship between the individual \( \pi \)-channels along the direction of the lamellar stacking. To avoid confusion, it has to be noted that the lamellar motif is used to represent the pattern, being different from the lamellar stacking (Scheme 1).

Electrostatic interaction and direct interaction have been proposed to account for the formation of \( \pi \)-stacking. In the former, the electron density of conjugated systems is modulated by the attaching substituent, thus giving rise to the variation in the electrostatic interactions between conjugated systems.\(^21–25\) The latter stresses that direct interactions exist between the substituent and the conjugated...
system along with the interactions induced from the change in bond polarity because of the presence of the substituent.\textsuperscript{26–30} It has been examined experimentally and theoretically that the direct interaction model is usually dominant for the $\pi$-stacking.\textsuperscript{31,32} The direct interaction could be associated with the enhanced London dispersion force.\textsuperscript{32} On the other hand, the occurrence of lamellar stacking is often rationalized by the compatibility principle, that is, like dissolves like. On account of the polarity difference between the conjugated and aliphatic moieties, the separation takes place accordingly. It is instinctive to relate the polarity effect with the electrostatic interaction.

Combination of the extended transition-state (ETS) method\textsuperscript{42–44} and the natural orbitals for chemical valence (NOCV) theory,\textsuperscript{45–47} coined as ETS–NOCV, has been employed to decompose the interaction energy ($\Delta E_{\text{int}}$) between two molecular entities into three chemically meaningful components—electrostatic interactions ($V_{\text{ele}}$), Pauli repulsion ($E_{\text{Pauli}}$), and orbital interactions ($E_{\text{oi}}$). $V_{\text{ele}}$ is the conventional electrostatic interaction between two molecules. $E_{\text{Pauli}}$ is the repulsive Pauli interaction between the occupied orbitals of two different molecules. $E_{\text{oi}}$ stands for the stabilizing interactions between the occupied molecular orbitals in one molecule and the unoccupied molecular orbitals in the other molecule along with the interaction of occupied and virtual orbitals within the same molecule in the final geometry. Because traditional density functionals often fail in describing the dispersion force accurately, an additional dispersion correction ($E_{\text{dis}}$) can be included in the above energy decomposition scheme with the aim of taking long-range interactions into consideration.\textsuperscript{48–56} Herein, numerous $N$,N'-dialkyl-1,4,5,8-naphthalenetetracarboxylic diimides (R-NDIs) are chosen for the study, such as $R = \text{C}_{14}\text{H}_{29}$,\textsuperscript{57} $\text{C}_{12}\text{H}_{25}$,\textsuperscript{58} $\text{C}_{8}\text{H}_{13}$,\textsuperscript{59} $\text{C}_{6}\text{H}_{11}$,\textsuperscript{60} $\text{C}_{4}\text{H}_{9}$,\textsuperscript{58} $\text{C}_{6}\text{H}_{5}$,\textsuperscript{61} and 1-CH$_3$C$_8$H$_{12}$\textsuperscript{58} (Scheme 2). The $\pi$- and lamellar stacking extracted from selected single-crystal structures are examined by ETS–NOCV. The interactions between NDI and the alkyl chain are also investigated computationally. The stacking principles on $\pi$- and lamellar stacking for R-NDIs are thus established. Moreover, in conjunction with R-NDIs, additional organic architectures containing a variety of conjugated functionalities and substituents are examined as well. The total sampling scope is up to 108 conjugated molecules. It is envisioned that the principles should apply to other organic semiconductors, paving the way for ultimate morphological control.

**Results and Discussion**

$\pi$-Stacking. It can be concluded from all the examined crystal structures that in the $\pi$-stacking, each R-NDI molecule is basically enclosed by 6 equiv. $\text{C}_{14}\text{H}_{29}$-NDI is taken for illustration (Figure 1). Symmetry operation reveals that the basic alignments between the central $\text{C}_{14}\text{H}_{29}$-NDI and the surroundings can be classified into three types and the corresponding intermolecular interactions between two molecules are labeled as $T_x$, $T_y$, and $T_q$ (Figure 1a). Figure 1b demonstrates the distinct separation of the conjugated and aliphatic moieties in the $\pi$-stacking from another viewpoint. Originally, the BP86/TZP level of theory was used to estimate $T_x$, $T_y$, and $T_q$. However, in the absence of $E_{\text{dis}}$ the interactions are commonly repulsive, being contrary to the formation of these single crystals. BP86-BJDAMP/TZP with the inclusion of Grimme’s BJDAMP dispersion correction was applied instead.\textsuperscript{30} ETS–NOCV results of $\pi$-stacking in $\text{C}_{14}\text{H}_{29}$-NDI are summarized in Table 1. In the parenthesis following $T_x$ ($x = a, p$, or $q$), NDI denotes that the aliphatic chains are replaced by four hydrogens and R denotes that the NDI groups are substituted by four hydrogens. $T_x$(NDI) and $T_x$(R) are utilized to give rough estimation about the individual contribution of conjugated and aliphatic moieties to the $\Delta E_{\text{int}}$. Several conclusions can be drawn from Table 1: (1) $E_{\text{dis}}$ > $V_{\text{ele}}$ > $E_{\text{oi}}$, is found for most decompositions, (2) $E_{\text{dis}}$ is the principal stabilization for either $T_x$, $T_y$, or $T_q$ (3) $T_y$ has the strongest stabilization ($\sim 37.00$ kcal mol$^{-1}$, entry 1, Table 1), followed by $T_q$ ($\sim 28.97$ kcal mol$^{-1}$, entry 4, Table 1) and $T_x$ ($\sim 23.46$ kcal mol$^{-1}$, entry 7, Table 1), (4) comparison of $T_y$(NDI) and $T_y$(R) reveals that the contribution of the tetradecanoyl group to the $\Delta E_{\text{int}}$ is comparable to that of the NDI functionality, and

![Figure 1](image)

**Table 1. ETS–NOCV Results of the $\pi$-Stacking in $\text{C}_{14}\text{H}_{29}$-NDI in kcal mol$^{-1}$**

| entry | type | $\Delta E_{\text{int}}$ | $E_{\text{Pauli}}$ | $V_{\text{ele}}$ | $E_{\text{oi}}$ | $E_{\text{dis}}$ |
|-------|------|------------------------|------------------|----------------|----------------|----------------|
| 1     | $T_x$ | $-37.00$               | $31.20$          | $-10.71$       | $-8.04$        | $-49.45$       |
| 2     | $T_y$(NDI) | $-18.02$        | $13.54$          | $-6.36$        | $-4.36$        | $-20.84$       |
| 3     | $T_y$(R) | $-15.02$            | $16.19$          | $-3.28$        | $-3.46$        | $-24.47$       |
| 4     | $T_p$ | $-28.97$               | $23.46$          | $-8.09$        | $-6.48$        | $-37.86$       |
| 5     | $T_q$(NDI) | $-6.96$           | $5.41$           | $-2.12$        | $-1.67$        | $-8.58$        |
| 6     | $T_q$(R) | $-16.79$            | $12.33$          | $-3.44$        | $-3.22$        | $-22.46$       |
| 7     | $T_q$ | $-7.79$                | $5.34$           | $-5.27$        | $-3.06$        | $-5.80$        |
| 8     | $T_q$(NDI) | $-5.96$           | $4.95$           | $-5.40$        | $-1.95$        | $-3.56$        |
| 9     | $T_q$(R) | $-0.94$            | $0.19$           | $0.11$         | $-0.10$        | $-1.14$        |

$\Delta E_{\text{int}} = E_{\text{Pauli}} + V_{\text{ele}} + E_{\text{oi}} + E_{\text{dis}}$. $^b$Percentage of total stabilization.

**Scheme 2. Chemical Structure of R-NDI**

![Scheme 2](image)

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to the summarized in Table 2. The principal character of dispersion are listed in the Supporting Information (Tables S1 moieties are not trivial. It is envisaged that the packing mode decreases from $C_{5}H_{11}-NDI$, $C_{4}H_{9}-NDI$, $C_{2}H_{5}-NDI$, and $1-CH_{3}C_{6}H_{12}-NDI$ − the NDI unit (see entries 5

fl linear and chain.

rectangular and rigid con

gets shorter. Both observations can be justified by the reduction in the molecular contact as the shortening of side chain.

structurally speaking, R-NDI consists of two primary units, that is, the R and NDI groups (Scheme 2). The R group has a linear and flexible molecular shape. The NDI group has yet a rectangular and rigid configuration. For a given space with a finite number of R-NDI molecules, the molecules would arrange themselves to gain maximal intermolecular interactions, of which the dispersion is the most dominant. As mentioned previously, the dispersion is linked with the molecular contact. It is thus envisioned that the dispersion stabilization of the whole system can be maximized by the closest packing. For R-NDIs, as a result of their disparity in the molecular shape, the R and NDI groups would undergo nanoscopic phase separation to accomplish the closest packing (Figure 1b). Along this line, the formation of π-stacking might stem essentially from the similarity in the shape rather than the polarity. It can be regarded as the consequence deriving from the governing role of dispersion over electrostatic interaction. However, it is recognized that molecular steric hindrance is associated with $E_{Pauli}$ which would prevent two molecules from establishing too compact stacking. For instance, in Table 3, two $C_{4}H_{3}NDI$ molecules are forced to align face-to-face and the resultant $\Delta E_{stap}$ are all repulsive irrespective of the variation in the intermolecular distance from 3.4 to 4.2 Å, being attributed to the drastically large value of $E_{Pauli}$. Moreover, as

| entry | distance (Å)$^{a}$ | $\Delta E_{int}$ | $E_{Pauli}$ | $V_{int}$ | $E_{stap}$ | $E_{Total}$ |
|-------|------------------|-----------------|-------------|-----------|------------|-------------|
| 1     | 3.4              | 1847            | 3800        | −1161     | −669       | −123        |
| 2     | 3.6              | 944             | 2166        | −703      | −409       | −111        |
| 3     | 3.8              | 496             | 1227        | −415      | −216       | −99         |
| 4     | 4.0              | 256             | 716         | −249      | −123       | −88         |
| 5     | 4.2              | 130             | 437         | −153      | −76        | −78         |

$^{a}$Distance between the two $C_{14}H_{29}-NDI$ molecules.

judged by the degree of stabilization, $V_{int}$ and $E_{stap}$ should still be able to regulate the molecular position in the π-stacking to a certain extent. Nonetheless, their dominance is just much inferior to $E_{stap}$.

### Lamellar Stacking

Single-crystal structures confirm that $C_{14}H_{29}-NDI$, $C_{12}H_{25}-NDI$, $C_{6}H_{13}-NDI$, $C_{4}H_{9}-NDI$, and $1-CH_{3}C_{6}H_{12}-NDI$ fall into the category of the lamellar motif (Scheme 1a), whereas $C_{6}H_{13}-NDI$ and $C_{4}H_{9}-NDI$ exhibit the herringbone motif (Scheme 1b). With the aim of investigating the intermolecular interactions in the lamellar stacking, we intentionally set a nonhydrogen intermolecular distance of 4 Å as a criterion. For a R-NDI molecule in one π-stacking channel, only the R-NDI molecule in the adjacent π-stacking locating close to or within 4 Å is considered to likely give rise to noticeable intermolecular interactions. On the basis of this definition, in the lamellar stacking, there are two corresponding interacting modes for $C_{14}H_{29}-NDI$, $C_{12}H_{25}-NDI$, and $C_{6}H_{13}-NDI$, three modes for $C_{4}H_{9}-NDI$ and $1-CH_{3}C_{6}H_{12}-NDI$, and four modes for $C_{4}H_{9}-NDI$ and $C_{6}H_{13}-NDI$ (Figure S1). For illustration, the ETS−NOCV results of $C_{4}H_{9}-NDI$ are listed in Table 4. $E_{stap}$ is still the major stabilization in the $\Delta E_{int}$. Nevertheless, modes a and b both exhibit much weaker stabilization than $T_{p}$, $T_{q}$ or $T_{s}$ in the π-stacking (Table 1).

Similar results are also observed for $C_{14}H_{29}-NDI$, $C_{12}H_{25}-NDI$, $C_{6}H_{13}-NDI$, $C_{4}H_{9}-NDI$, and $1-CH_{3}C_{6}H_{12}-NDI$ (Tables S7−S12). Overall, most of the interactions in the

| $T_{p}$ | $T_{q}$ | $E_{stap}$ | $E_{Pauli}$ | $E_{Total}$ |
|--------|--------|------------|-------------|-------------|
| −37.00 | −7.79  | −49.45 (73%) | −37.86 (73%) | −5.80 (44%) |
| −35.46 | −7.76  | −47.36 (71%) | −34.42 (71%) | −5.74 (42%) |
| −23.99 | −7.44  | −28.65 (70%) | −16.74 (72%) | −7.09 (50%) |
| −22.59 | −8.62  | −26.65 (66%) | −19.62 (68%) | −7.75 (47%) |
| −22.10 | −6.57  | −26.39 (62%) | −10.92 (66%) | −4.33 (39%) |
| −20.83 | −5.96  | −24.26 (65%) | −10.14 (65%) | −3.77 (34%) |
| −21.64 | −3.29  | −26.40 (70%) | −25.87 (70%) | −4.92 (69%) |

$^{a}$Percentage of total stabilization.
shorter than the pentanyl one, C4H9-NDI is expected to adopt
NDI seems to be an exception. Given that the butyl group is
the total stabilization are much smaller than those resulting from
C2H5-NDI belong to this group. Figure 2 clearly shows that in
observation. In Table S10, the interactions of C4H9-NDI in the
a herringbone motif, which is yet not the experimental
lamellar stacking can be up to
7.70 kcal mol
ΔE
−
π
-int
E
π
oi
E
dis
3.17
−3.16
−0.76 (12%)
−0.85 (13%)
−4.72 (75%)
−0.55
1.53
−0.24 (12%)
−0.40 (19%)
−1.44 (69%)

Table 4. ETS–NOCV Results of the Lamellar Stacking in C14H29-NDI in kcal mol

Figure 2. Deviation of the pentanyl group from the stable zigzag configuration in the C6H11-NDI crystal.

the crystal structure of C6H11-NDI, the pentanyl group deviates from the stable zigzag configuration to reduce the dimension of lamellar stacking, leading to the formation of a herringbone motif. In contrast, the long or bulky alkyl chains, such as C14H29, C12H25, C6H13, and 1-CH3C6H12, would preclude R-NDI molecules from the herringbone motif and the lamellar motif would be realized instead. Nevertheless, C6H13-NDI seems to be an exception. Given that the butyl group is shorter than the pentanyl one, C6H13-NDI is expected to adopt a herringbone motif, which is yet not the experimental observation. In Table S10, the interactions of C6H13-NDI in the lamellar stacking can be up to −7.70 kcal mol
ΔE
−
π
-int
E
π
oi
E
dis
18659

Figure 3. Intercalation of the butyl chains in the lamellar stacking in the C6H13-NDI crystal.

stabilization, accounting for the construction of a lamellar motif for C6H13-NDI.

Interactions between NDI and the Alkyl Chain. The π-stacking and lamellar stacking are investigated individually hitherto. It is intriguing to further look into the interactions between NDI and the alkyl chain. Nevertheless, the corresponding crystal structures are not experimentally accessible. Theoretical approaches are employed instead. Geometry optimizations were performed between the NDI molecule and various alkanes at the BP86-BJ DAMP/TZP level of theory. The minimum nature of each optimized geometry was confirmed by frequency calculation. The computational results reveal that the NDI molecule is able to form stable adducts with different alkanes and E
ΔE
-dis
still plays the most important role (Table 5). The results strongly suggest that the interactions between NDI and the alkyl chain can be substantial, especially for the extensive alkyl chain, which again challenges the conventional point of view that a conjugated moiety interacts barely with an aliphatic chain. As expected, the ΔE
ΔE
-int
E
π
oi
ΔE
-dis
Delta
E
ΔE
-dis
18662

Figure 3. Intercalation of the butyl chains in the lamellar stacking in the C6H13-NDI crystal.

General Applicability. With the intention of examining the general applicability of the closest packing model derived from the governing character of dispersion, additional 101 organic crystals comprising various conjugated functionalities and substituents are investigated by ETS–NOCV as well. Molecular pairs extracted from the crystal structures were calculated, and the ΔE
ΔE
-int
E
π
oi
ΔE
-dis
Delta
E
ΔE
-dis
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**THEORETICAL METHODS**

All calculations were performed with ADF 2016. BP86 density functional is selected as the computational method. Triple zeta with 1 polarization function (TZP) is the basis set. Grimme’s BJDAMP is used for dispersion correction. Geometry optimization was carried out at the same level of theory mentioned above. The minimal nature of all optimized structures is examined by frequency computation. Cartesian coordinates are listed in the Supporting Information.

**CONCLUSIONS**

ETS–NOCV has been performed to study the π- and lamellar stacking for a series of R-NDI crystals. The energy decomposition results indicate that the dispersion is the most important stabilization in the intermolecular interactions. The increase in the molecular contact should in principle strengthen the dispersion. The closest packing model for R-NDIs is thus rational to see that the R and NDI groups undergo nanoscopic phase separation in the developed. It is envisaged that the established principles provide rationalization for the use of long and branch side chains to increase the solubility for conjugated molecules and polymers by hindering the π-stacking. As for the lamellar stacking, the corresponding interactions are much smaller than those resulting from the π-stacking. In order to achieve maximal stabilization, to reduce the length of lamellar stacking and leave more space for the π-stacking is a straightforward approach, which would lead to the herringbone motif. In contrast, the long or bulky alkyl chains would prohibit R-NDIs from the herringbone motif, and the closest packing model would be realized instead. It has to be emphasized that Pauli repulsion would restrain two molecules from establishing too compact stacking and the closest packing model has its limitation. Moreover, the interactions between NDI and the alkyl chain are examined. The NDI molecule is able to form stable adducts with different alkanes, and the interactions between NDI and the alkyl chain can be substantial, especially for the extensive alkyl chain. The results provide rationalization for the use of long and branch side chains to increase the solubility for conjugated molecules and polymers by hindering the π-stacking. Along with R-NDIs, additional organic crystals comprising various conjugated functionalities and substituents are also investigated by ETS–NOCV. The sampling scope is up to 108 conjugated molecules. The dominant role of dispersion force irrespective of the variation in the conjugated moieties and substituents is further confirmed. It is envisaged that the established principles are applicable to other organic semiconductors. The traditional perspective toward the π- and lamellar stacking might be modified, paving the way for ultimate morphological control.

**ETSY—NOCV Results of the Optimized Adducts between the NDI and Various Molecules in kcal mol⁻¹**

| entry | molecule       | ΔE_{add} | E_{add} | V_{dd} | E_{di} | E_{di} |
|-------|---------------|----------|---------|--------|--------|--------|
| 1     | ethane        | −4.79    | 6.4     | −2.15  | (19%)  | −1.9   | (17%)  | −7.14 | (64%)  |
| 2     | hexane        | −8.96    | 11.65   | −4.35  | (21%)  | −3.28  | (16%)  | −12.98| (63%)  |
| 3     | 2-methyl-pentane | −8.45  | 11.22   | −3.93  | (20%)  | −3.19  | (16%)  | −12.55| (64%)  |
| 4     | 3-methyl-pentane | −9.28  | 12.81   | −4.61  | (21%)  | −3.59  | (16%)  | −13.89| (63%)  |
| 5     | 2,2-dimethyl-butane | −8.21 | 11.36   | −4.03  | (21%)  | −3.31  | (17%)  | −12.23| (62%)  |
| 6     | 2,3-dimethyl-butane   | −9.06  | 12.32   | −4.40  | (21%)  | −3.48  | (16%)  | −13.50| (63%)  |
| 7     | tetradeacene   | −13.36  | 17.22   | −7.51  | (25%)  | −4.88  | (16%)  | −18.19| (59%)  |
| 8     | NDI           | −24.52  | 28.25   | −11.5  | (22%)  | −8.31  | (16%)  | −32.96| (62%)  |

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02713.

ETS–NOCV results of π- and lamellar stacking in C₆H₁₃-NDI, C₉H₁₇-NDI, C₉H₁₇-NDI, C₉H₁₇-NDI, C₆H₁₃-NDI, and 1-CH₂C₆H₁₃-NDI in kcal mol⁻¹; interacting modes in the lamellar stacking for C₁₂H₂₅-NDI; C₁₃H₂₇-NDI, C₁₂H₁₇-NDI, C₁₂H₁₇-NDI, C₁₅H₁₇-NDI, 1-CH₂C₁₂H₂₁-NDI, C₁₂H₁₇-NDI, and C₁₂H₁₇-NDI; ETS–NOCV results in kcal mol⁻¹ for the molecular pairs in 101 organic crystals; and Cartesian coordinates of the optimized structures (PDF)

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Notes
The authors declare no competing financial interest.

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