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Correlation of mobility and molecular packing in organic transistors based on cycloalkyl naphthalene diimides[†]

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A series of cycloalkyl-substituted naphthalene tetracarboxylic diimides (Cyn-NTCDIs, n = 3-8) are prepared and the transistor properties and molecular packings are systematically investigated. Cy5–Cy8-NTCDIs have similar brickwork structures, where two molecules are located on the top of a molecule with large displacement along the molecular *short* axis. The intermolecular overlap is maximized when the small slipping along the molecular *long* axis makes the molecules nearly perpendicular to the substrate. Consequently, the mobility decreases exactly in the same order as the interlayer *d*-spacings.

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Introduction

Naphthalene tetracarboxylic diimide (NTCDI, Scheme 1) is a representative n-type organic semiconductor,1-11 and in particular the cyclohexyl derivative (Cy6-NTCDI, Scheme 1) shows an electron mobility as high as 6.2 cm² V⁻¹ s⁻¹,¹¹ which is one of the highest among the n-type organic field-effect transistors. In contrast, the n-hexyl derivative (n6-NTCDI, Scheme 1) shows an electron mobility of only 0.1 cm² V⁻¹ s⁻¹.¹¹ In order to achieve high performance in organic transistors, control of the molecular packing and the thin-film morphology is important.¹¹⁻¹⁴ Many perylene tetracarboxylic diimides (PTCDI) adopt π -stacking structures,¹⁵ where the slips along the molecular long axis (longitudinal offset) and the molecular short axis (transverse offset) determine the intermolecular transfer.^{2,16} It has been pointed out that not only the simple molecular overlap but also the molecular orbital nodes influence the band broadening and the resulting crystallochromism.16 In contrast, halogenated PTCDIs form a large variety of molecular packings from the π -stacking to the herringbone structure.¹⁷ Many halogenated NTCDIs have a π -stacking structure, and the intermolecular interaction is essentially onedimensional.¹⁸ In contrast to these PTCDIs and NTCDIs, cyclohexyl NTCDI has a brickwork structure (see Fig. 4),^{2,19} where all molecules are parallel to each other, but instead of

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forming the usual stacking structure, two molecules are equivalently located on the top of a molecule. In this face-toface overlap, the molecules are slipped largely along the molecular *short* axis, and the resulting intermolecular interactions run in two diagonal directions. Molecular orbital calculation has revealed that this diagonal interaction is important in the brickwork structure.²⁰

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Among the NTCDI derivatives, long alkyl substituted NTCDI derivatives have been investigated extensively,^{21,22} but cycloalkyl substituted NTCDI derivatives are limited. In the present work, we have prepared various cycloalkyl NTCDIs (Cyn-NTCDIs, n = 3-8, Scheme 1) and investigated the crystal structures, thinfilm properties, and transistor characteristics. We have previously investigated intermolecular interaction in the herringbone structure by continuously changing the intermolecular geometry, and demonstrated that the dihedral angle has crucial importance in determining the charge transport.²³ From a similar systematic investigation, here we demonstrate that the crucial factor that determines the transistor performance in the brickwork structure is the molecular tilt angle, which is governed by the slipping distance along the molecular *long* axis in the overlapped molecules.



Scheme 1 Chemical structure of NTCDI derivatives.

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[†] Electronic supplementary information (ESI) available: Additional information on synthesis, redox properties, UV-vis spectra, single crystal structures, device fabrication, theoretical calculations, and packing of the cycloalkyl group. CCDC 939277–939280. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3tc30920g

Results and discussion

Synthesis

The Cy*n*-NTCDIs were prepared following the reported procedure (Scheme 2) by direct condensation of naphthalene dianhydride with the appropriate amines.²⁴ 1,4,5,8-Naphthalenetetracarboxylic acid anhydride, cycloalkylamine, and a catalytic amount of zinc acetate were heated in quinoline at 140–150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol. The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation.

Electrochemical property

In order to estimate the energy levels of the present semiconductors, cyclic voltammograms (CV) and the ultravioletvisible (UV-vis) spectra were measured. The optical band gaps of *Cyn*-NTCDIs were determined from the absorption edge of the UV-vis absorption spectra (Fig. 1). The electrochemical data are summarized in Table 1. Although alkyl groups are different, their electrochemical properties are very similar. The lowest



Scheme 2 Synthesis of NTCDI derivatives



Fig. 1 UV-vis spectra of Cyn-NTCDIs.

Table T Electrochemical properties of Cyn-MCDIs						
Cyn	$^{a}E_{\mathrm{red}}\left(\mathrm{eV}\right)$	$^{b}E_{\text{LUMO}}$ (eV)	$^{c}E_{\mathrm{HOMO}}\left(\mathrm{eV}\right)$	$^{d}\lambda_{abs}\left(nm ight)$	$e_{E_{g}}(eV)$	
Cy4	-1.11	-4.13	-7.33	387	3.20	
Cy5	-1.15	-4.09	-7.27	390	3.18	
Cy6	-1.18	-4.06	-7.24	390	3.18	
Cy7	-1.14	-4.10	-7.28	390	3.18	
Cy8	-1.17	-4.07	-7.25	390	3.18	

Electrochemical properties of Cup NTCDI2

^{*a*} From cyclic voltammogram using Bu₄NPF₆ in CH₂Cl₂ *vs.* AgNO₃. ^{*b*} LUMO levels are estimated by the relationship, $E_{LUMO} = -5.24 \text{ eV} - E_{red}$.^{*z*} ^{*c*} Estimated by $E_{HOMO} = E_{LUMO} - E_g$. ^{*d*} From optical absorption data in CH₂Cl₂. ^{*e*} E_g : optical gap. unoccupied molecular orbital (LUMO) levels are located around -4.1 eV, which is low enough to achieve the electron transport.²⁵

Crystal structures

Single crystals of Cyn-NTCDIs were obtained by slow evaporation of toluene solutions. Cy3-NTCDI showed poor solubility, and good quality crystals were not obtained. Therefore, singlecrystal X-ray structure analyses were carried out for Cy4–Cy8-NTCDIs. Crystallographic data are listed in Table 2. Cy4-NTCDI takes a packing different from the other compounds, but other Cy5–Cy8-NTCDIs show similar packing motifs.

The crystal structure of Cy4-NTCDI is shown in Fig. 2. Cy4-NTCDI has one crystallographically independent molecule in a unit cell. All molecular planes are parallel and the stack is strongly dimerized. The directions of the long axes in the dimer molecules are, however, not parallel to each other (Fig. 2(b)). A short intermolecular C–O contact of 3.14 Å is observed in the dimer. The transfer integral exists only along the stacking (*c*) axis, indicating one-dimensional conduction. The transfer integral *c*1 (*c*1 = 127 meV) is much larger than the other one (*c*2 = 7.7 meV) to indicate remarkable dimerization.

The crystal structure of Cy6-NTCDI has been reported previously.11,19 The crystal structure analyses are carried out for Cy5, Cy7, and Cy8-NTCDIs. The packing motifs are depicted in Fig. 3-6. Cy5-Cy8-NTCDI molecules are located on inversion centers so that half the molecule is crystallographically independent. Except for Cy8-NTCDI, the NTCDI planes are parallel to each other. The molecules, however, do not make the usual stacking structure. Another molecule located on the side of a molecule exists on the same plane, but the next "stacked" molecule is located in between these two molecules. Although the usual stacking structure forms a face-to-face overlap using nearly the whole molecular plane, the brickwork structure makes a face-to-face overlap using half the molecular plane, and the remaining half is used to construct the interaction with another molecule. Since the interplanar spacings in these two face-to-face overlaps are nearly the same (see Table 5), the two molecules are located in the same plane in a good approximation. Cy6-NTCDI shows high symmetry, and the geometry to these two molecules in the next layer is exactly the same (Fig. 4). Consequently, the interaction p forms a square lattice in the two-dimensional conducting layer. Cy5- and Cy7-NTCDIs have non-equivalent interactions, a and c (Fig. 3 and 5), but these two construct a similar two-dimensional network. The transfer integrals are later discussed in connection with Table 5. Cy8-NTCDI shows a distorted brickwork structure (Fig. 6), where the molecular planes are not parallel to each other, but tilted with a dihedral angle of 16.8°.

Thin-film properties

Atomic force microscopy (AFM) images of the thin films evaporated on *n*-octyltrichlorosilane (OTS)-treated SiO₂/Si are shown in Fig. 7. The thin-film of Cy3-NTCDI consists of small domains with typical dimensions of $0.3 \times 1 \ \mu\text{m}^2$ (Fig. 7a), while the Cy8-NTCDI film is composed of long microcrystals with typically

 R_1 (%)

6.69

Cyn	Cy4	Cy5	Cy6 ^a	Cy7	Cy8	
Chemical formula	$C_{22}H_{18}N_2O_4$	$C_{24}H_{22}N_2O_4$	$\mathrm{C}_{26}\mathrm{H}_{26}\mathrm{N}_{2}\mathrm{O}_{4}$	$C_{28}H_{30}N_2O_4$	$C_{30}H_{34}N_2O_4$	
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	
Molecular weight	374.40	402.45	—	458.56	486.61	
Space group	C2/c	$P\bar{1}$	C2/m	$P\bar{1}$	$P2_{1}/c$	
a (Å)	27.567	6.0407	8.541	6.211	19.385	
<i>b</i> (Å)	9.156	16.75	6.678	17.454	7.905	
<i>c</i> (Å)	13.752	5.2404	18.4279	5.236	8.96	
α (°)	_	98.72	_	90.85	_	
β (°)	97.93	104.53	102.479	100.77	97.38	
γ (°)	—	74.8	—	94.3	—	
$V(Å^3)$	3437.86	493.223	1026.19	555.809	1222.12	
Ζ	8	1	2	1	2	
$D (g cm^{-3})$	1.447	1.355		1.370	1.322	

6.65

6.64

Table ? Crystallographic data of Cyn-NTCDIs

5.09 ^a The crystallographic data are taken from the previous report.^{11,19}



Fig. 2 Crystal structure of Cy4-NTCDI, (a) viewed along the b axis, (b) overlap mode viewed from the top of the molecular plane, and (c) the packing motif.



Fig. 3 Crystal structure of Cy5-NTCDI, (a) viewed along the molecular long axis, (b) viewed from the top of the molecular plane, and (c) the overlap modes.

 $0.5 \times 3 \,\mu\text{m}^2$ size (Fig. 7f). For large *n*-cycloalkanes, the grain size tends to increase. Cy6-NTCDI is an exception, in which flat homogeneous regions with clear stripes are obtained.

Thin films of Cyn-NTCDIs show clear X-ray diffraction (XRD) peaks as shown in Fig. 8, from which the d-spacings are extracted as summarized in Table 3. The d-spacing of Cy6-NTCDI is in good agreement with the crystallographic c axis and



12.09

Fig. 4 Crystal structure of Cy6-NTCDI, (a) viewed along the molecular long axis, (b) viewed from the top of the molecular plane, and (c) the overlap modes.¹⁹



Fig. 5 Crystal structure of Cy7-NTCDI, (a) viewed along the molecular long axis, (b) viewed from the top of the molecular plane, and (c) the overlap modes.



Fig. 6 Crystal structure of Cy8-NTCDI, (a) viewed along the molecular long axis, (b) viewed from the top of the molecular plane, and (c) the overlap modes.



Fig. 7 AFM images of Cyn-NTCDIs.



Fig. 8 XRD profiles of Cyn-NTCDIs.

Table 3 XRD peaks and d-spacings of Cyn-NTCDIs

Cyn-NTCDI	2 heta (°)	<i>d</i> (A)		
Cy3	6.93	12.77		
Cy4	6.23	14.20		
Cy5	5.49	16.10		
Cy6	4.91	18.00		
Cy7	5.09	17.36		
Cy8	5.19	17.03		

the conducting ab plane is parallel to the substrate (Fig. 4). Accordingly, the molecular long axis of Cy6-NTCDI is perpendicular to the substrate. This is because the molecular long axis of Cy6-NTCDI coincides with the crystallographic c axis (Fig. 4b). The d-spacings of Cy5 and Cy7-NTCDIs also agree well with the crystallographic b axes (Table 2), and the conducting acplanes are nearly parallel to the substrate. However, the molecular long axes are not exactly perpendicular to the substrate, and tilted to some extent. This is because the molecular long axis is considerably tilted from the crystallographic b axis (Fig. 3b and 5b). Cy8-NTCDI is also tilted considerably (Fig. 6). As a consequence, Cy6-NTCDI exhibits the largest d-spacing, whereas other materials show smaller d-spacings (Table 3).

Transistor characteristics

After vacuum deposition of Cv3-Cv8-NTCDIs on OTS-treated SiO₂/Si substrates, transistors with top-contact Au electrodes were fabricated. The transistor characteristics were measured both under vacuum and in air. The transfer characteristics are shown in Fig. 9. The mobility (μ) and threshold voltage (V_{TH}) are summarized in Table 4 and Fig. 10. All compounds including Cy3-NTCDI and Cy8-NTCDI show n-type transistor characteristics, among which Cy6-NTCDI shows the highest mobility of $0.52 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under vacuum. In air, the mobility drops to some extent (0.11 cm² V⁻¹ s⁻¹) and V_{TH} increases from 44 to 61 V. Comparing the measurements under the same conditions, the mobility of these materials makes a peak at Cy6-NTCDI (Fig. 12), whereas the $V_{\rm TH}$ values are approximately the same except for Cy7-NTCDI. It is relatively difficult to attain small $V_{\rm TH}$ values in these materials,11 but we have achieved V_{TH} values around 40 V under vacuum. These transistors are operated even in air, though the mobilities are reduced, and $V_{\rm TH}$ increases typically from about 40 V to 60 V.

Intermolecular interactions

In Cy5–Cy8-NTCDIs with a brickwork structure, all molecules are parallel, and as shown in Fig. 11 the intermolecular geometry is defined by the displacements along the long and short axes within the molecular plane. We consider that a nitrogen atom represents the position of a molecule, and the nitrogen atom of the nearby molecule is projected onto the molecular plane of the reference molecule as indicated by the blue lines. Within the reference molecular plane, the direction of the long axis is defined as the *x* axis, and the perpendicular direction as the *y* axis. Then the positions of the *P* and *Q* points are represented by the *x* and *y* coordinates (D_x and D_y).



Fig. 9 Transfer characteristics of (a) Cy3-, (b) Cy4-, (c) Cy5-, (d) Cy6-, (e) Cy7-, and (f) Cy8-NTCDI transistors measured at $V_D = 60$ V under vacuum (solid curves) and in air (dashed curves).

Table 4 Transistor properties of Cyn-NTCDIs

Cyn-NTCDI	Condition	$\mu ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$V_{\mathrm{TH}}\left(\mathbf{V}\right)$	On/off ratio
Cv3	Vacuum	$5.0 imes10^{-3}$	43	$2 imes 10^4$
- 5 -	Air	$6.3 imes10^{-4}$	76	$1 imes 10^3$
Cy4	Vacuum	0.013	48	$5 imes 10^3$
2	Air	$2.1 imes 10^{-3}$	90	$1 imes 10^3$
Cy5	Vacuum	0.011	38	$5 imes 10^4$
•	Air	$9.1 imes 10^{-4}$	62	$2 imes 10^4$
Cy6	Vacuum	0.52	44	$1 imes 10^6$
	Air	0.11	61	$1 imes 10^6$
Cy7	Vacuum	0.019	89	$3 imes 10^5$
•	Air	$1.9 imes10^{-3}$	122	$1 imes 10^4$
Cy8	Vacuum	0.018	20	$3 imes 10^3$
•	Air	$9.4 imes10^{-4}$	61	$1 imes 10^3$



Fig. 10 Alkyl dependence of mobility and V_{TH} in Cyn-NTCDIs. Closed symbols represent measurements under vacuum and open symbols are those in air.



Fig. 11 Intermolecular geometry with the definition of the long and short axes.

The displacements, the transfer integrals, and the interplanar spacings are summarized in Table 5. It is characteristic that D_y is about 4 Å for all NTCDI face-to-face interactions, but D_x changes largely. In particular, D_x of Cy6-NTCDI is comparatively small. The interplanar spacings Δ are typically 3.3–3.4 Å but slightly dependent on the crystals.

As shown in Table 5, transfer integrals between the molecules located on approximately the same molecular plane are less than one tenth of the face-to-face interactions. The main interactions are mediated by the face-to-face interactions, which make a two-dimensional network owing to the brickwork molecular arrangement (Fig. 3–6).^{19,20} When there are two interactions t_a and t_p , the bandwidth is obtained from $4t_a + 4t_p$.²⁴ The calculated transfer integrals of 20–50 meV lead to a bandwidth of 150–300 meV.

Cyn- NTCDI	Direction	D_x (Å)	Dy (Å)	Interplanar distance ⊿ (Å)	Transfer integral (meV)
Cv5	c	1.12	3.99	3.22	35
-,-	a	2.85	4.02	3.48	55
	p^a	3.97	8.01	_	1.5
Cy6	p	0.82	4.19	3.34	19
	a^a	1.64	8.38	_	3
Cy7	с	0.98	4.06	3.22	25
	а	2.93	3.95	3.80	26
	p^a	3.91	8.01	_	1.5
Cy8	p1	1.41	3.43	—	39
	p2	1.95	4.3	—	39
	c ^a	3.36	7.73	—	0

^{*a*} Interactions between the molecules located on approximately the same molecular plane. Others are slipped face-to-face interactions.

Two-dimensional map of the transfer integral

In order to estimate the overlap between two parallel molecules, we have carried out density functional theory (DFT) calculation. The molecular orbital (MO) of methyl NTCDI is calculated by a Gaussian 09 program at the B3LYP/6-31G(d,p) level.²⁸ The LUMO spreads over the whole NTCDI core (inset in Fig. 12), but does not have population on the atoms located on the long axis because of the orbital symmetry.

The overlap integral is calculated as a function of (D_x, D_y) in the two-dimensional plane (Fig. 12) for a fixed interplanar spacing, $\Delta = 3.4$ Å. Since the interplanar spacings in the actual crystals are slightly different from this value, the individual transfer integrals in Table 5 are somewhat different from the values in the two-dimensional map. Positive transfer integral regions are designated in green, and negative regions in red, but the absolute magnitude is important to make an energy band. The displacements in the actual Cy*n*-NTCDIs are plotted in the two-dimensional map. When D_x or D_y increases, the transfer integral decreases with oscillation. The periodicity of the



Fig. 12 Two-dimensional map of the transfer integral (eV) in NTCDIs (Cyn and *n*6) and PTCDIs (*n*4-P and *n*5-P).

oscillation in the D_{y} direction is about 2.4 Å, which is equal to the width of an aromatic ring. All Cyn-NTCDI compounds are located around $D_v = 4$ Å. This corresponds to the displacement of one and half aromatic rings; the typical overlap is depicted in Fig. 11. The oscillation along D_x is less clear because the LUMO is stripe-like in this direction (Fig. 12). At $D_r = 0$, the side C=C bond is located approximately on the top of an aromatic ring of the adjacent molecule (Fig. 4b). This is a ring-over-bond geometry, which is known to maximize the intermolecular overlap by minimizing the intermolecular repulsion at the same time.²⁹ The calculated transfer integral has a maximum around $D_x = 2.8$ Å, at which a C=C bond is placed on the top of another C=C bond. This is an eclipsed geometry. Although the calculated overlap becomes large, this is not an actually favored geometry. The periodicity of D_x corresponds to the length of an aromatic ring, that is about 2.8 Å.

Correlation between mobility and molecular arrangement

As shown in Fig. 8, Cy6-NTCDI shows the smallest θ value, and Cy7- and Cy8-NTCDIs are the next, followed by Cy5-NTCDI. This order is exactly the same as the order of the mobility. Cy6-NTCDI has the largest *d*-spacing, because the molecular long axis is perpendicular to the substrate, but other NTCDIs have smaller *d*-spacings, in which the direction of the molecular long axis is tilted from the perpendicular direction. Here the ring size does not have a principal importance particularly from Cy5 to Cy7-NTCDIs, but the tilt angle is mainly important. If the molecule is perpendicular to the substrate, D_x is 0 Å, and D_x increases as the molecule is more tilted. Accordingly, Cy6-NTCDI with the smallest D_x shows the highest mobility, and the mobility seems to be a simple decreasing function of D_x . This contrasts with the calculated transfer integral shown in Fig. 12, which makes a maximum around $D_x = 2.8$ Å. Different from the stacking structure, the intermolecular overlap in the brickwork structure is small due to the large slip of $D_{y} = 4$ Å. The charge transport, expected from the mobility, seems to be determined by the simple molecular overlap without considering the molecular orbitals.¹⁶ Consequently, the mobility is a simple decreasing function of D_x , which is simply related to the *d*spacing and the tilt angle.

In the stacking structure, the standing geometry has been frequently reported to be most favorable for charge transport as well. In the tilted arrangement, misfit on the domain boundary has been pointed out to be the origin of the reduced charge transport. The densely packed characteristic morphology in Cy6-NTCDI observed by AFM (Fig. 7d) may be related to this scenario. In such a case, the difference of the transfer integral is not the principal factor to determine the mobility. The perfectly two-dimensional square-lattice-like arrangement is another favorable factor to the charge transport in Cy6-NTCDI.

It is, however, notable that all Cy5–Cy8-NTCDIs basically adopt the brickwork structure, though the molecular packing is slightly distorted from the ideal symmetry in Cy6-NTCDI. In general, alkyl-NTCDI and PTCDI tend to have π -stacking structures. For example, the *n*-hexyl derivative (*n*6-NTCDI) has a similar face-to-face stack with (D_x , D_y) = (1.18 Å, 3.52 Å) with

 $\Delta = 3.20$ Å,¹¹ but the second face-to-face interaction is so largely displaced ($D_x = 6.29$ Å) that a one-dimensional π -stacking structure is realized instead of the brickwork structure. Butyl(n4)-PTCDI and pentyl(n5)-PTCDI have stacking structures with $(D_x, D_y) = (3.07 \text{ Å}, 1.26 \text{ Å})$ and (3.12 Å, 1.02 Å), respectively, with $\Delta = 3.40$ Å.¹⁵ Therefore, the short-axis displacement D_{ν} is small with the relatively large long-axis displacement D_x . As a consequence, the interaction is large only in the stacking direction, and the molecular interaction is one dimensional. High mobility has been reported in fluorocarbon (C₄F₇H₂-) substituted dicyano-PTCDI not only in the thin films (0.6 cm² $V^{-1} s^{-1}$) but also in the single crystals (6 cm² V⁻¹ s⁻¹).^{30,31} In this compound, two molecules are located on the top of a molecule, where one molecule has a geometry $(D_x, D_y) = (0.47 \text{ Å}, 4.08 \text{ Å})$ with $\Delta = 3.24$ Å that is very close to the present brickwork structure. However, another molecule has a considerably displaced geometry $(D_x, D_y) = (3.65 \text{ Å}, 6.41 \text{ Å})$ with $\Delta = 3.29 \text{ Å}$. This is an intermediate between the brickwork and π -stacking structures, and the relatively small anisotropy (transfer integrals: 35 and 19 meV) is related to the reported high mobility. There is a large degree of freedom in the stacking manner of NTCDI and PTCDI molecules because these molecules have large aromatic planes, but high mobility is attained in cycloalkyl-NTCDIs due to the two-dimensional brickwork structure.

In-plane geometry

Fig. 13 depicts two parallel molecules on the same plane moved along D_x by fixing D_y . A geometry with no displacement ($D_x =$ 0 Å) is not favorable because of the repulsion of the hydrogen atoms (Fig. 13a). When the NTCDI molecule is moved half the benzene ring, namely by $D_x = 1.4$ Å (Fig. 13b), the geometry is favorable due to the reduced hydrogen-hydrogen repulsion as well as the interaction between the carbonyl oxygen and the hydrogen. The actual hydrogen–oxygen distance is 2.6 Å, which is not recognized as a hydrogen bond, but the weak interaction is expected. Further translation with a benzene ring distance $(D_x = 2.8 \text{ Å})$ is unfavorable (Fig. 13c), and translation with one and a half rings ($D_x = 4.2$ Å) is favorable (Fig. 13d). The displacement (D_x) of two molecules in the same plane is obtained from the sum of two face-to-face D_x values as shown in Table 5. The interaction *a* in Cy6-NTCDI is located around $D_x =$ 1.6 Å. The interactions p in Cy5- and Cy7-NTCDIs are located around $D_x = 4$ Å. The actual system takes the stable geometries of either Fig. 13b or 13d. This is the reason that $D_x = 0.82$ Å is not exactly zero even in Cy6-NTCDI. Since this in-plane D_x determines the face-to-face D_x 's and consequently the molecular tilt angles as well as the *d*-spacings, the small slip shown in



Fig. 13 Possible geometries of two NTCDI molecules in the same plane.

Fig. 13b is considered to be the origin of the high mobility. For Cy8-NTCDI, however, the molecular planes are not exactly parallel to each other, and the so obtained $D_x = 3.36$ Å does not exactly correspond to the stable geometry.

Conclusions

Although the stacking manner of NTCDI and PTCDI molecules has a large degree of freedom owing to the large aromatic planes, the molecular packing is, in many cases, a one-dimensional π -stacking structure. However, the present cycloalkyl-NTCDIs realize the two-dimensional brickwork structure, where two molecules are equivalently located on the top of a molecule. Among the brickwork packings, the displacement along the molecular long axis (D_x) is the crucial factor that determines the transistor performance. The mobility shows a maximum at Cy6-NTCDI near $D_x = 0$ Å, and the order of the mobility is exactly the same as that of the d-spacing in XRD. Cy6-NTCDI has the largest *d*-spacing, which is associated with the small displacement D_x and the molecular long axis nearly perpendicular to the substrate. Small displacement D_x is also important because the perpendicular arrangement minimizes the misfit between the domain boundaries.

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