Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

IR cavity ringdown spectroscopy and density functional calculation theory of pyrrole – diethyl ketone clusters: Impacts of carbon-chain flexibility on a diversity of N-H…O=C hydrogen bond

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S1. Integrated band intensities of the observed NH stretch

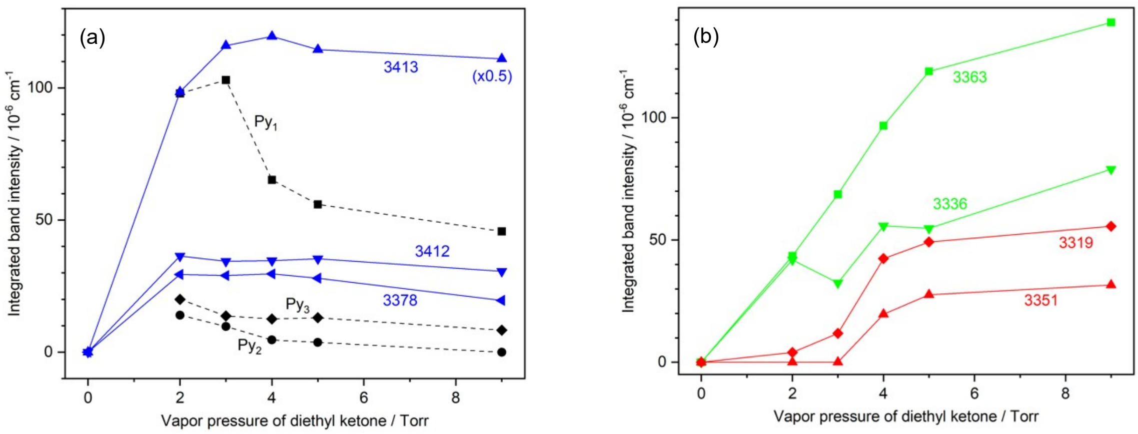


Fig. S1 Integrated band intensities of the NH stretch as a function of the vapor pressure of Dek. (a) Py_1 – Py_3, Py_1-Dek_1 (3413 cm^{-1}) and Py_2-Dek_1 (3412 and 3378 cm^{-1}). (b) Py_1-Dek_2 (3363 and 3336 cm^{-1}) and higher clusters (3351 and 3319 cm^{-1}).

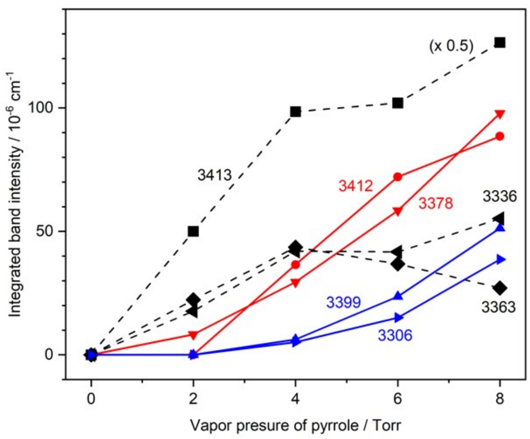
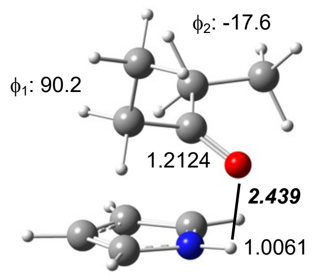


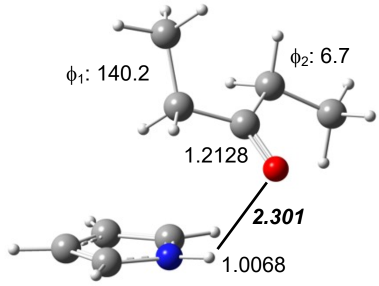
Fig. S2 Integrated band intensities of the NH stretch for Py-Dek clusters as a function of the vapor pressure of pyrrole.

S2. Calculated isomeric structures of Py-Dek cluster

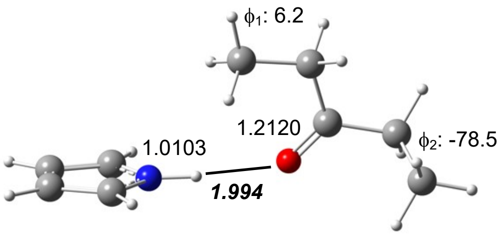
S2-1. Py_1-Dek_1



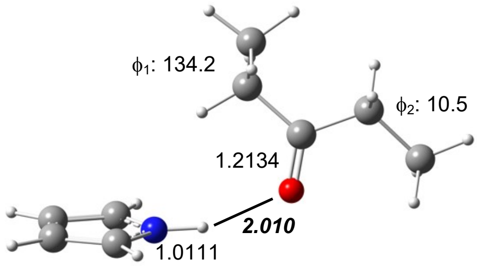
Py_1-$Dek(g')_1$(II) (5.55, 24.51)



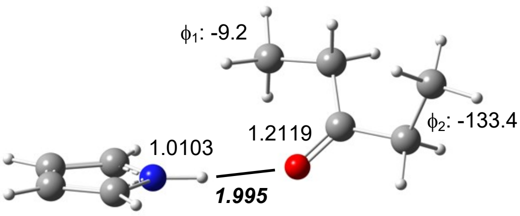
Py_1-$Dek(g'')_1$(II) (5.92, 23.36)



Py_1-$Dek(g')_1$(III) (6.09, 23.97)



Py_1-$Dek(g'')_1$(III) (6.26, 23.02)



Py_1-$Dek(g'')_1$(IV) (7.02, 22.27)

Fig. S3 Higher-energy isomers of Py_1-Dek_1 calculated at the M05-2X/6-311+G(d,p) level. Isomers are classified by a conformation of Dek, such as anti (a), gauche1 (g') and gauche2 (g"). Roman numbers of I, II… indicate the order of energetic stability in each conformation. Two values in parentheses are the relative and binding energy with a unit of kJ/mol. Geometric parameters of bond lengths (N-H, C=O, and N-H…O) and dihedral angles (C-C-C=O) are inserted with units of Å and degree, respectively.

S2-2. Comparison with Py_1-Ac_1 and Py_1-Cp_1

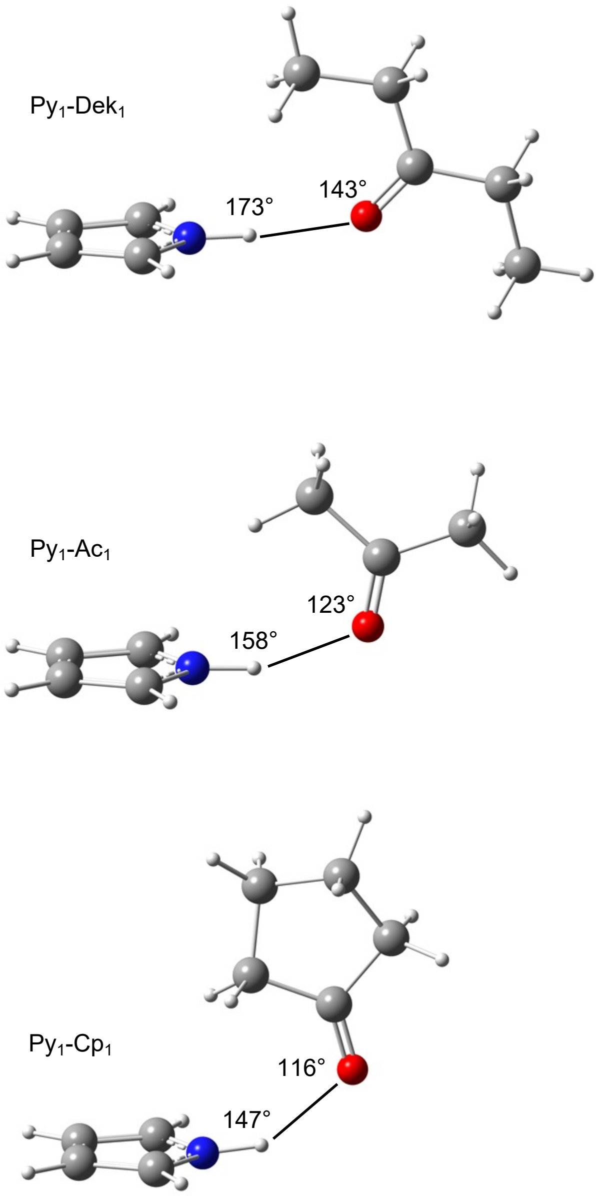
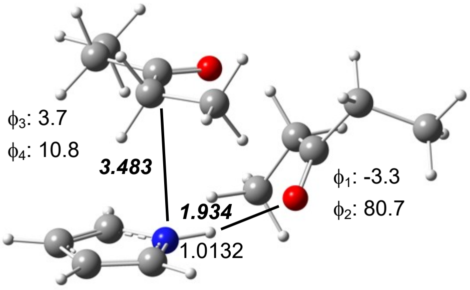
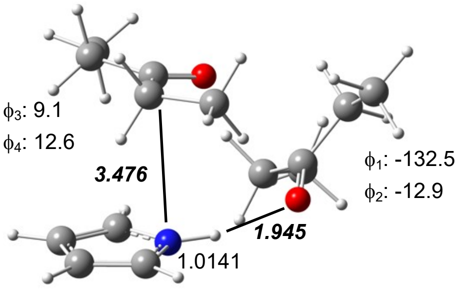


Fig. S4 Optimized N-H…O=C H-bond structures of Py_1-Dek_1, -Ac_1, and -Cp_1 calculated at the M05-2X/6-311+G(d,p) level. Two values in each structure are the intermolecular angles of N-H…O and H…O=C. At a first glance, the NH and CO groups are quasi-parallel in Py_1-Dek_1, but almost perpendicular in Py_1-Ac_1 and -Cp_1.

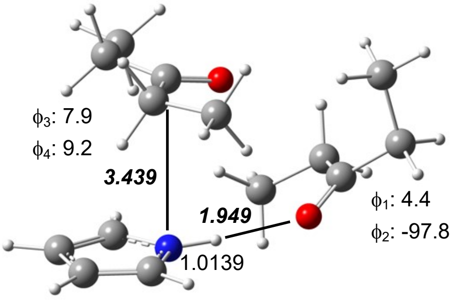
S2-3. Py_1-Dek_2



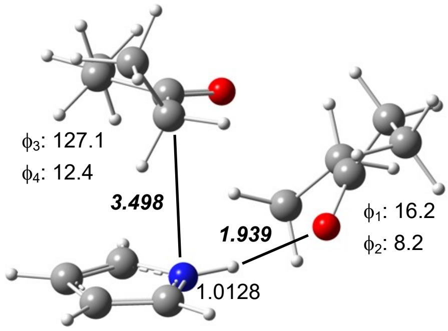
(a) Py_1-Dek(g'-a)$_2$(II) (*6.76*, 63.92)



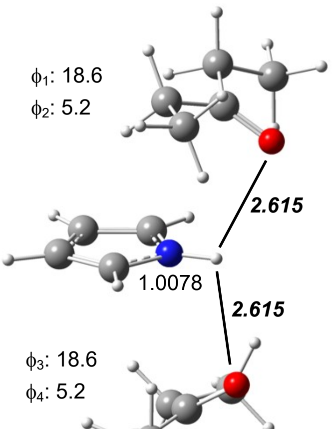
(b) Py_1-Dek(g"-a)$_2$(I) (*7.34*, 62.56)



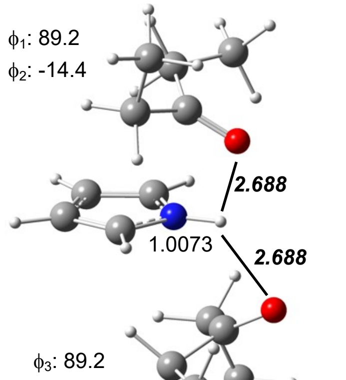
(c) Py_1-Dek(g'-a)$_2$(III) (*8.19*, 62.49)



(d) Py_1-Dek(a-g")$_2$(I) (*8.52*, 61.33)



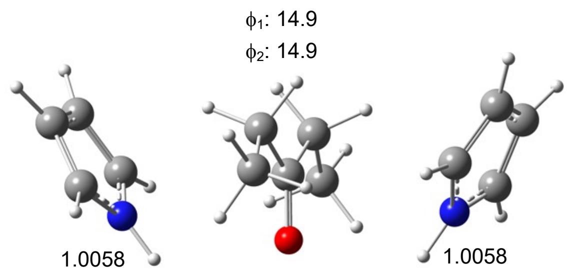
(e) Py_1-Dek(a-a)$_2$(II) (*21.08*, 44.56)



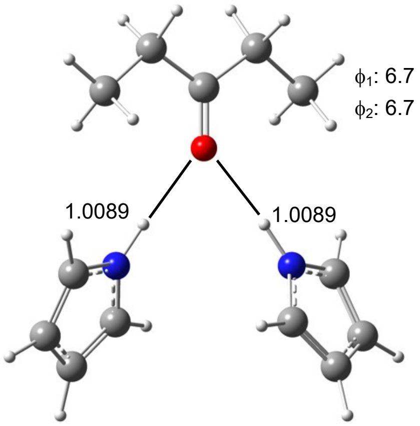
(f) Py_1-Dek(g'-g')$_2$(II) (*31.50*, 44.23)

Fig. S5 Six isomeric structures of Py_1-Dek_2 with higher energy calculated at the M05-2X/6-311+G(d,p) level. Isomeric structures are classified by a combination of Dek conformation, such as Dek(a-a). Roman numbers of I, II and so on, indicate the order of energetic stability in each conformation. Two values in parentheses are the relative energy (italic) and the binding energy (roman) with a unit of kJ/mol. Geometric parameters of bond lengths (N-H, C=O, N-H…O, and C…N) and dihedral angles (C-C-C=O) are inserted with units of Å and degree, respectively.

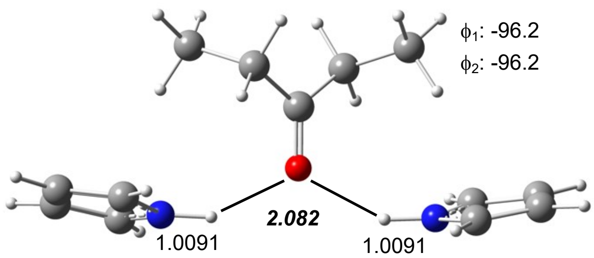
S2-4. Py_2-Dek_1



Py_2-Dek(a)$_1$(II) (*21.58*, 46.68)



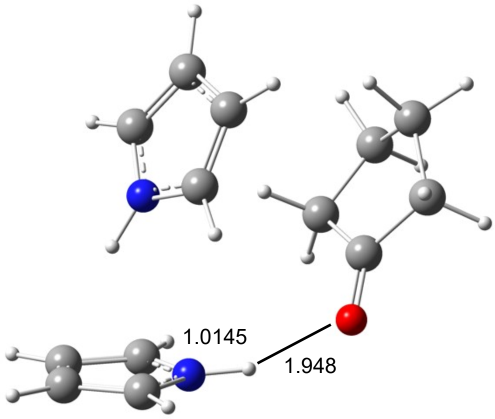
Py_2-Dek(a)$_1$(III) (*23.20*, 45.05)



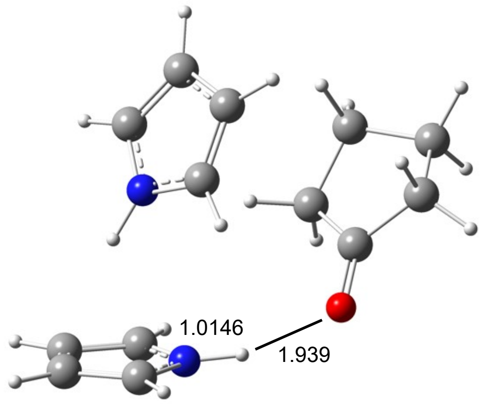
Py_2-Dek(g'g')$_1$(I) (*27.91*, 51.43)

Fig. S6 Three isomeric structures of Py_2-Dek_1 with higher energy calculated at the M05-2X/6-311+G(d,p) level. Isomeric structures are classified by a conformation of Dek, such as anti (a), gauche1 (g') and gauche2 (g"). Roman numbers of I, II and so on, indicate the order of energetic stability in each conformation. Two values in parentheses are the relative energy (italic) and the binding energy (roman) with a unit of kJ/mol. Geometric parameters of bond lengths (N-H and N-H…O) and dihedral angles (C-C-C=O) are inserted with units of Å and degree, respectively.

S2-5. Comparison with Py_2-Cp_1



Py_2-Cp_1 (Cy-A(2))



Py_2-Cp_1 (Cy-A(5))

Fig. S7 Optimized cyclic structures of Py_2-Cp_1 calculated at the M05-2X/6-311+G(d,p) level. Geometric parameters of the NH bond lengths and NH…O intermolecular distances are inserted with units of Å. The notations of Cy-A(2) and Cy-A(5) are taken from the reference "Y. Matsumoto and K. Honma, IR cavity ringdown spectroscopy and density functional theory for jet-cooled pyrrole-cyclopentanone binary clusters: Effect of pseudorotation on N-H⋯O═C hydrogen bonds, *J. Phys. Chem. A*, 2020, **124**, 2436–2448."

S3. Calculated vibrational frequency of Py-Dek clusters

S3-1. Py_1-Dek_1, Py_1-Dek_2, Py_2-Dek_1

Table S1 Calculated NH stretches of Py-Dek clusters, performed at the M05-2X/6-311+G(d,p) level. The scaling factor for anharmonicity correction is 0.9393. Units of relative energy, binding energy, frequency, and IR intensity are kJ/mol, kJ/mol, cm^{-1}, and km/mol, respectively.

	Relative energy	*Binding energy*	*Calculated frequency (IR intensity)*	*Assignment*	*Structure*
Py_1-Dek_1	*0.00*	*25.01*	*3478 (118)*	*Free*	*Py_1-Dek(a)$_1$ (I)*
	0.40	*25.01*	*3412 (637)*	*HB (O=C)*	*Py_1-Dek(a)$_1$ (II)*
	2.88	*27.18*	*3393 (395)*	*HB (O=C)*	*Py_1-Dek(g')$_1$ (I)*
	3.41	*25.87*	*3451 (166)*	*Quasi-free*	*Py_1-Dek(g")$_1$ (I)*
	5.55	*24.51*	*3485 (112)*	*Free*	*Py_1-Dek(g')$_1$ (II)*
	5.92	*23.36*	*3472 (136)*	*Free*	*Py_1-Dek(g")$_1$ (II)*
	6.09	*23.97*	*3405 (642)*	*HB (O=C)*	*Py_1-Dek(g')$_1$ (III)*
	6.26	*23.02*	*3388 (561)*	*HB (O=C)*	*Py_1-Dek(g")$_1$ (III)*
	7.02	*22.27*	*3400 (651)*	*HB (O=C)*	*Py_1-Dek(g")$_1$ (IV)*
Py_1-Dek_2	*0.00*	*65.63*	*3361 (564)*	*HB (O=C)*	*Py_1-Dek(a-a)$_2$ (I)*
	5.13	*65.55*	*3351 (587)*	*HB (O=C)*	*Py_1-Dek(a-g')$_2$ (I)*
	6.38	*64.30*	*3335 (632)*	*HB (O=C)*	*Py_1-Dek(g'-a)$_2$ (I)*
	6.76	*63.92*	*3349 (620)*	*HB (O=C)*	*Py_1-Dek(g'-a)$_2$ (II)*
	7.34	*62.56*	*3332 (626)*	*HB (O=C)*	*Py_1-Dek(g"-a)$_2$ (I)*
	8.19	*62.49*	*3334 (656)*	*HB (O=C)*	*Py_1-Dek(g'-a)$_2$ (III)*
	8.52	*61.33*	*3349 (598)*	*HB (O=C)*	*Py_1-Dek(a-g")$_2$ (I)*
	21.08	*44.56*	*3464 (113)*	*Free*	*Py_1-Dek(a-a)$_2$ (II)*
	31.50	*44.23*	*3474 (97)*	*Free*	*Py_1-Dek(g'-g')$_2$ (I)*
Py_2-Dek_1	*0.00*	*68.26*	*3386 (365)* *3421 (440)*	*HB (O=C)* *HB (π)*	*Py_1-Dek(a)$_1$ (I)*
	5.93	*66.60*	*3309 (565)* *3414 (406)*	*HB (O=C)* *HB (π)*	*Py_1-Dek(g")$_1$ (I)*
	21.58	*46.68*	*3485 (90)* *3486 (116)*	*Free* *Free*	*Py_1-Dek(a)$_1$ (II)*
	23.20	*45.05*	*3415 (276)* *3428 (723)*	*HB (O=C)* *HB (O=C)*	*Py_1-Dek(a)$_1$ (III)*
	27.91	*51.43*	*3415 (719)* *3422 (28)*	*HB (O=C)* *HB (O=C)*	*Py_1-Dek(g'g')$_1$ (I)*

S3-2. Py_1-Dek_3 and Py_2-Dek_2

Table S2 Calculated NH stretches of Py_1-Dek_3 and Py_2-Dek_2 hetero-tetramers at the M05-2X/6-311+G(d,p) level. The scaling factor used is 0.9393. Units of frequency and IR intensity are cm^{-1} and km/mol, respectively.

		Frequency	*IR intensity*	*Assignment*
Py_1-Dek_3	*Py_1-Dek(a-a-a)$_3$*	*3344*	*523*	*N-H…O=C*
	Py_1-Dek(g'-a-a)$_3$	*3264*	*665*	*N-H…O=C*
	Py_1-Dek(a-g'-a)$_3$	*3321*	*564*	*N-H…O=C*
Py_2-Dek(a)$_2$	*(I)*	*3312* *3317*	*1* *1585*	*Sym.* *Asym.*
	(II)	*3363* *3408*	*423* *362*	*N-H…π* *N-H…O=C*
	(III)	*3361* *3430*	*409* *434*	*N-H…π* *N-H…O=C*

S4. NBO analysis of Py_2-Dek_1 and Py_2-Cp_1

Table S3 The 2nd order perturbative energy ($E^{(2)}$ in kJ/mol) due to charge transfer interactions calculated by natural bond orbital (NBO) analysis for Py_2-Dek_1 and Py_2-Cp_1. The calculation is performed at the M05-2X/6-311+G(d,p) level.

	Py₂-Dek(a)₁ (I)	*Py₂-Dek(g")₁ (I)*	*Py₂-Cp₁ (Cy-A(2))*	*Py₂-Cp₁ (Cy-A(5))*
$n_O \rightarrow \sigma^*_{NH}$ [a]	*27.1*	*38.7*	*41.3*	*44.0*
$\pi_{CO} \rightarrow \sigma^*_{NH}$ [a]	*2.55*	*2.51*	*0.96*	*0.50*
$\pi_{CC} \rightarrow \sigma^*_{NH}$ [b]	*10.9*	*10.7*	*11.0*	*11.4*

[a] N-H…O=C H-bond

[b] N-H…π H-bond