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Supporting Information

"Local decomposition of imaginary polarizabilities and dispersion coefficients"

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1 Theory

1.1 Anisotropic Dispersion Interaction

We will here give the dispersion energy in a form which requires a few definitions in order to make the presentation self-contained. Consider two separated systems (molecules or atoms) labeled by 1 and 2. They have each a center-of-mass at a position represented by vectors $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, with Cartesian representations in a common coordinate system: X_1^i and X_2^i for $i = 1, 2, 3$. We refer to the vector connecting the two subsystems by

$$\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2 \tag{1}$$

i.e., the distance between the centers of mass is $R_{12} = |\mathbf{R}_{12}|$

We use $\mathbf{r}_1$ for an electronic coordinate associated with system 1 and $\mathbf{r}_2$ for electrons associated with system 2. The density-density response function of system 1 is defined by (see e.g. Ref. 1, eq 9.4.2)

$$\langle\langle \hat{\rho}(\mathbf{r}_1); \hat{\rho}(\mathbf{r}_1{}')\rangle\rangle_\omega^{(1)} = \sum_{n_1>0} \frac{\langle \Psi_0^{(1)}|\hat{\rho}(\mathbf{r}_1)|\Psi_{n_1}^{(1)}\rangle\langle \Psi_{n_1}^{(1)}|\hat{\rho}(\mathbf{r}_1{}')|\Psi_0^{(1)}\rangle}{\hbar(\omega - \omega_{n_1}^{(1)})} - \frac{\langle \Psi_0^{(1)}|\hat{\rho}(\mathbf{r}_1')|\Psi_{n_1}^{(1)}\rangle\langle \Psi_{n_1}^{(1)}|\hat{\rho}(\mathbf{r}_1)|\Psi_0^{(1)}\rangle}{\hbar(\omega + \omega_{n_1}^{(1)})} \tag{2}$$

where $\Psi_{n_1}^{(1)}$ is a stationary state of system 1 with $n_1 = 0$ being the ground state and $\hbar\omega_{n_1}^{(1)} \equiv E_{n_1}^{(1)} - E_0^{(1)}$ is excitation energy from the ground state of system 1 to its n_1:th excited state. The density operator $\hat{\rho}(\mathbf{r}_1)$ has the property that its expectation value is the electron density at a point in space. It is given in second-quantized form by expanding it in a given basis set on system 1, $\{\phi_p^{(1)}(\mathbf{r}_1)\}_{p=1}^\infty$:

$$\hat{\rho}(\mathbf{r}_1) = \sum_{pq} \phi_p^{(1)}(\mathbf{r}_1)^* \phi_q^{(1)}(\mathbf{r}_1)(a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}) \tag{3}$$

where $a_{p\alpha}^\dagger a_{q\alpha}$ is an operator representing an excitation of an α-electron (spin $+\frac{1}{2}$) from orbital q to p and $a_{p\beta}^\dagger a_{q\beta}$ the equivalent for a β-electron (spin $-\frac{1}{2}$).

In particular the dispersion energy of two interacting molecules (denoted by 1 and 2) is given by

$$E_{\text{disp}} = -\frac{\hbar}{2\pi} \iint \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \frac{1}{r_{12}} \iint \mathrm{d}\mathbf{r}'_1 \mathrm{d}\mathbf{r}'_2 \frac{1}{r'_{12}} \int_0^\infty \mathrm{d}\omega \langle\langle \hat{\rho}(\mathbf{r}_1); \hat{\rho}(\mathbf{r}'_1) \rangle\rangle^{(1)}_{\mathrm{i}\omega} \langle\langle \hat{\rho}(\mathbf{r}_2); \hat{\rho}(\mathbf{r}'_2) \rangle\rangle^{(1)}_{\mathrm{i}\omega} \tag{4}$$

where the linear response functions are evaluated at an imaginary frequency $\mathrm{i}\omega$. The intermolecular Coulomb potential can further be expanded in multipole moments, e.g., in solid spherical harmonics. Another alternative is a real-valued Taylor expansion to obtain the Cartesian moments, by expanding around the intermolecular distance vector. Introducing the electronic coordinate vectors relative to the local molecular coordinate frames (see Fig.S1) $\mathbf{r}_{1;1} = \mathbf{r}_1 - \mathbf{R}_1$ and $\mathbf{r}_{2;2} = \mathbf{r_2} - \mathbf{R}_2$ we have

$$\mathbf{r}_{12} = \mathbf{r}_{1;1} - \mathbf{r}_{2;2} + \mathbf{R}_{12} \tag{5}$$

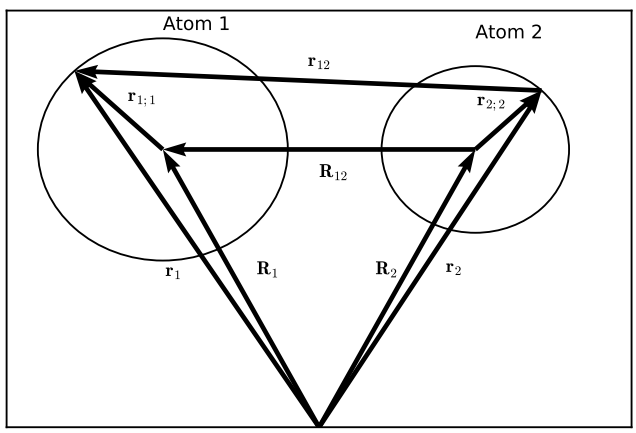

Figure S1: Definition of coordinates in section 2.1

When the first two terms are small compared to the last, as we can assume for long-range

intermolecular interactions, we may expand the Coulomb potential in a Taylor series

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_{1;1} - \mathbf{r}_{2;2} + \mathbf{R}_{12}|} = \sum_{n=0}^{\infty} \frac{1}{n!}((\mathbf{r}_{1;1} - \mathbf{r}_{2;2}) \cdot \nabla_{R_{12}})^n \frac{1}{R_{12}} \tag{6}$$

where the derivative operator only acts on the internuclear distance

$$\nabla_{R_{12}} = \left(\frac{\partial}{\partial X_{12}^1}, \frac{\partial}{\partial X_{12}^2}, \frac{\partial}{\partial X_{12}^3} \right) \tag{7}$$

Furthermore we can use the binomial theorem to obtain

$$((\mathbf{r}_{1;1} - \mathbf{r}_{2;2}) \cdot \nabla_{R_{12}})^n = \sum_{k=0}^{n} \binom{n}{k} (\mathbf{r}_{1;1} \cdot \nabla_{R_{12}})^k (-\mathbf{r}_{2;2} \cdot \nabla_{R_{12}})^{n-k} \tag{8}$$

Substituting expansions in Eqs. 6 and 8 in the linear response function in Eq. 2, we can rewrite Eq. 4 as

$$\begin{aligned} E_{\text{disp}} = &-\frac{\hbar}{2\pi} \sum_{nk} \sum_{n'k'} \frac{1}{n!n'!} \binom{n}{k} \binom{n'}{k'} (-1)^{n-k+n'-k'} \times \\ &\int_0^\infty \mathrm{d}\omega \langle\langle \int d\mathrm{r}_1 \hat{\rho}(\mathbf{r}_1)(\mathbf{r}_{1;1} \cdot \nabla_{R_{12}})^k; \int d\mathrm{r}_2 \hat{\rho}(\mathbf{r}_1')(\mathbf{r}_{1;1}' \cdot \nabla_{R_{12}'})^{k'} \rangle\rangle_{\mathrm{i}\omega} \times \\ &\langle\langle \int d\mathrm{r}_1' \hat{\rho}(\mathbf{r}_2)(\mathbf{r}_{2;2} \cdot \nabla_{R_{12}})^{n-k}; \int d\mathrm{r}_2' \hat{\rho}(\mathbf{r}_2')(\mathbf{r}_{2;2}' \cdot \nabla_{R_{12}'})^{n'-k'} \rangle\rangle_{\mathrm{i}\omega} \left. \frac{1}{R_{12}} \frac{1}{R_{12}'} \right|_{R_{12}=R_{12}'} \end{aligned} \tag{9}$$

where we can identify linear response functions of second-quantized formulations of multipole moments of various orders.

The lowest non-vanishing term is with $k = k' = 1$ and $n = n' = 2$, where we have electrical dipole operators

$$\hat{\mathbf{r}} = \int \mathrm{d}\mathbf{r} \hat{\rho}(\mathbf{r}) \mathbf{r} \tag{10}$$

and we can identify the well-known expression for dipole-dipole polarizabilities

$$\alpha(\mathrm{i}\omega) = -\langle\langle \hat{\mathbf{r}}; \hat{\mathbf{r}} \rangle\rangle_{\mathrm{i}\omega} \tag{11}$$

This expansion for a specific orientation of the molecules is an expression which couples the molecular polarizability tensors with second derivatives of the intermolecular distance and which decays as R_{12}^{-6}

$$E_{\mathrm{disp}} \approx -\frac{\hbar}{2\pi} \int_0^\infty \mathrm{d}\omega \sum_{ijkl} \alpha_{ij}^{(1)}(\mathrm{i}\omega)\alpha_{kl}^{(2)}(\mathrm{i}\omega) T_{ik} T_{jl} \tag{12}$$

where the summation is over cartesian coordinates in a common coordinate system, and T is the second-order derivative of the Coulomb potential

$$T_{ik} = \frac{\partial^2}{\partial X_{12}^i \partial X_{12}^k} \frac{1}{R_{12}} = \frac{3X_{12}^i X_{12}^k - \delta_{ik} R_{12}^2}{R_{12}^5} \tag{13}$$

1.2 Isotropic dispersion coefficient C_6

An isotropic expression for the dispersion energy is obtained by rotational averaging of the two subsystems independently. Molecular tensors such as polarizabilities are usually calculated in a coordinate system fixed by molecular nuclei (body-fix axes) whereas observations are carried out in a coordinate system defined by the observer (lab-fix axes). With $C_{\mu i}$ as the transformation matrix between body-fix (greek indices) and space-fix (roman indices) axes this averaging may be written

$$E_{\mathrm{disp}}^{\mathrm{iso}} \approx -\frac{\hbar}{2\pi} \int_0^\infty \mathrm{d}\omega \sum_{ijkl} \sum_{\mu\nu\sigma\tau} \alpha_{\mu\nu}^{(1)}(\mathrm{i}\omega)\alpha_{\sigma\tau}^{(2)}(\mathrm{i}\omega) \overline{C_{\mu i} C_{\nu j}} \quad \overline{C_{\sigma k} C_{\tau l}} T_{ik} T_{jl} \tag{14}$$

Detailed expressions for rotational averages of tensors can be found, e.g., in Ref. 2; in our case the average can be written as

$$\overline{C_{\mu i} C_{\nu j}} = \frac{1}{3} \delta_{\mu\nu} \delta_{ij} \tag{15}$$

Substituting with the isotropic polarizabilities

$$\bar{\alpha} = \frac{1}{3} \sum_k \alpha_{kk} \tag{16}$$

we obtain

$$\begin{aligned} E_{\text{disp}}^{\text{iso}}(R_{12}) &= -\frac{\hbar}{2\pi} \int_0^\infty \overline{\alpha}^{(1)}(\mathrm{i}\omega) \overline{\alpha}^{(2)}(\mathrm{i}\omega) \sum_{ik} T_{ik} T_{ik} \\ &= -\frac{\hbar}{2\pi} \int_0^\infty \overline{\alpha}^{(1)}(\mathrm{i}\omega) \overline{\alpha}^{(2)}(\mathrm{i}\omega) \frac{6}{R_{12}^6} \\ &= -\frac{3\hbar}{\pi} \int_0^\infty \bar{\alpha}^{(1)}(\mathrm{i}\omega) \bar{\alpha}^{(2)}(\mathrm{i}\omega) \mathrm{d}\omega \frac{1}{R_{12}^6} \\ &\equiv -\frac{C_6}{R_{12}^6} \end{aligned} \tag{17}$$

which defines the well-known C_6 coefficient for the dispersion interaction. By decomposing the molecular polarizabilities $\alpha^{(1)}$ and $\alpha^{(2)}$ into distributed atomic contributions $\alpha_i^{(1)}$ and $\alpha_j^{(2)}$, respectively, where i is an atomic site in molecule 1 and j an atomic site in molecule 2, the atom-atom dispersion coefficient C_6^{ij} for atoms i and j can be written as

$$C_6^{ij} = \frac{3\hbar}{\pi} \int_0^\infty \bar{\alpha}_i^{(1)}(\mathrm{i}\omega) \bar{\alpha}_j^{(2)}(\mathrm{i}\omega) \mathrm{d}\omega \tag{18}$$

where now the distributed polarizabilities for the atoms contributes to the atomic C_6^{ij} dispersion. Note that in order to calculate the total dispersion energy by our scheme LoProp (see below), each atom-atom pair has to be evaluated. For a water dimer with 3 atoms in each molecule, there is thus $3 \times 3 = 9$ atom-pairs to consider. This is due to the LoProp polarizability being additive and summing up to the molecular polarizability, and the sum

of all LoProp C_6^{ij} elements being equal to the molecular C_6.

2 Basis set dependence

Table S1: Cartesian coordinates (in Å) of formaldehyde optimized at the B3LYP/6-31++G** level

C	0.000000	0.000000	-0.000208
O	0.000000	0.000000	1.209275
H	0.941309	0.004318	-0.585533
H	-0.941309	-0.004318	-0.585533

Table S2: Cartesian coordinates (in Å) of formamide optimized at the B3LYP/6-31++G** level

C	-0.146425	-0.001816	0.140187
O	-0.335276	-0.004158	1.345032
N	1.078514	0.013368	-0.453411
H	-0.975567	-0.012092	-0.592741
H	1.909426	0.023666	0.121870
H	1.175529	0.014573	-1.457146

Table S3: Cartesian coordinates (in Å) of glycine optimized at the B3LYP/6-31++G** level

N	0.012280	-0.299019	-0.005567
C	1.269704	0.014326	-0.662389
C	2.406693	0.036981	0.354098
O	2.241321	0.185991	1.539527
H	1.488307	-0.733613	-1.437762
H	1.296150	1.002244	-1.158173

H	0.019011	0.064036	0.944621
H	-0.781435	0.087603	-0.504101
O	3.662001	-0.064871	-0.155404
H	3.639128	-0.233439	-1.109051

3 Diatomics

3.1 H2 dimer

Table S4: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

H	0.00000	0.00000	-0.37070
H	0.00000	0.00000	0.37070

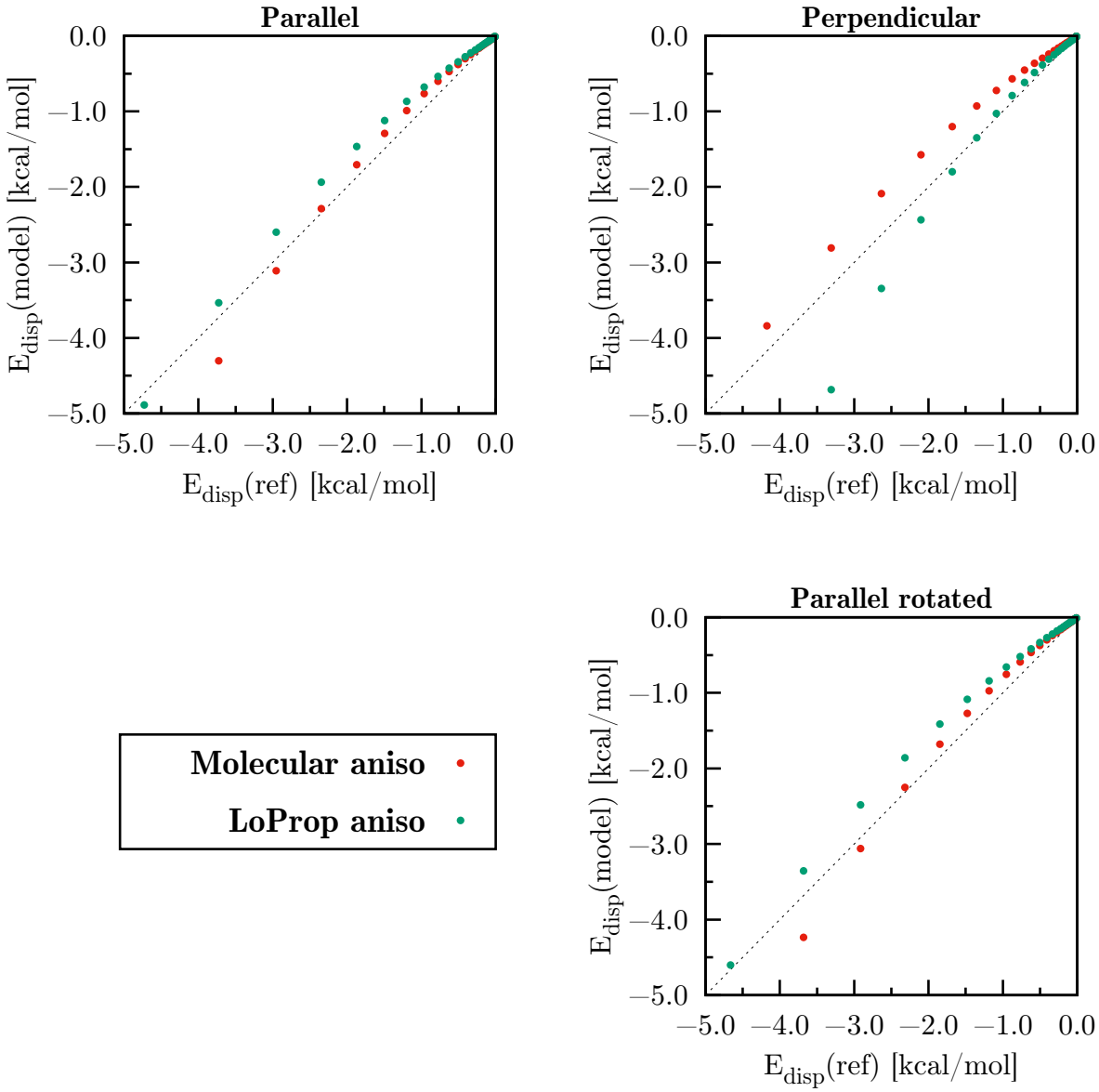

Figure S2: Scatter plots of the dispersion energy for the H_2–H_2 dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

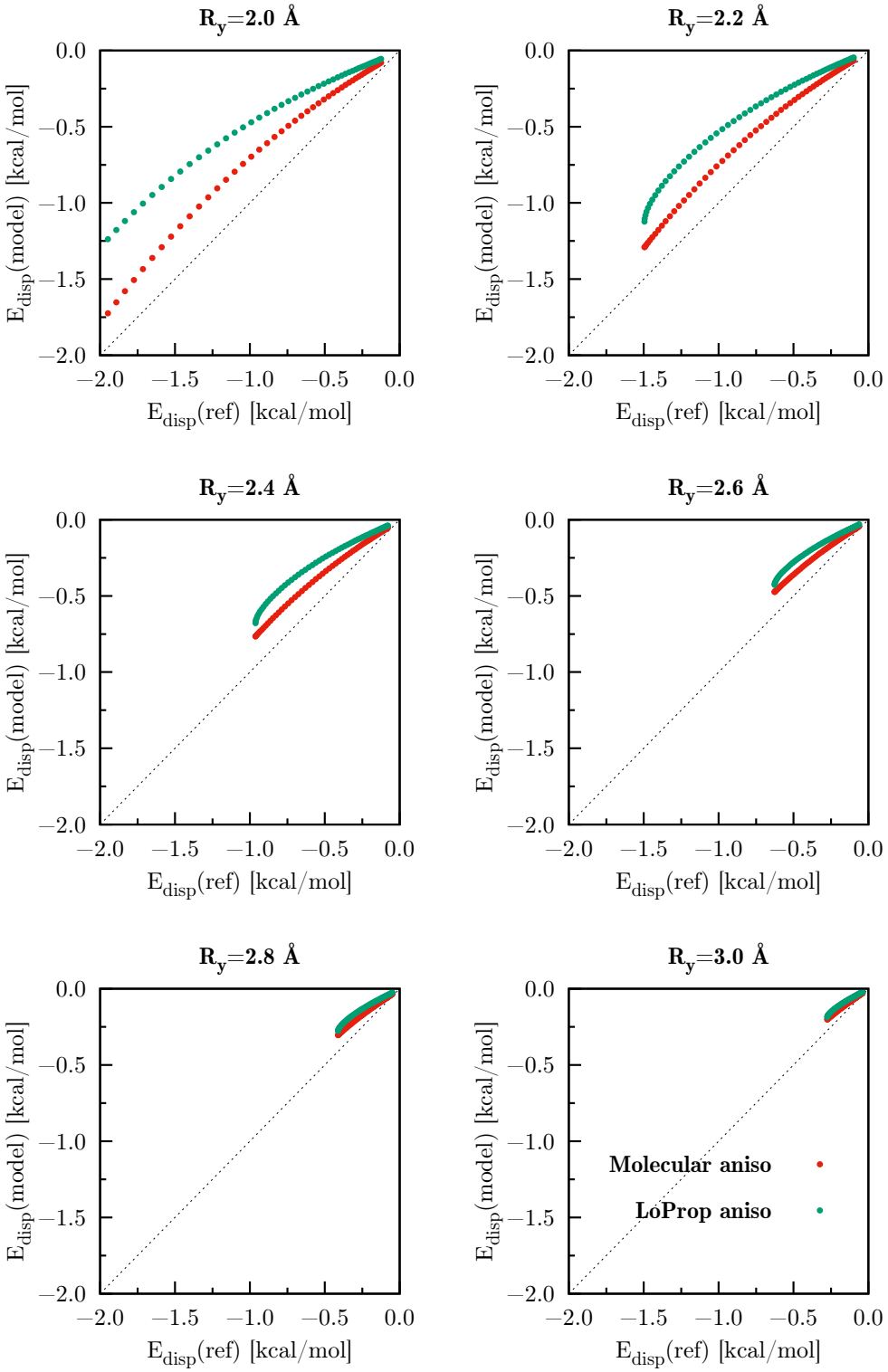

Figure S3: Scatter plots of the dispersion energy for the H_2–H_2 dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

3.2 N2 dimer

Table S5: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

N	0.00000	0.00000	0.55256
N	0.00000	0.00000	-0.55256

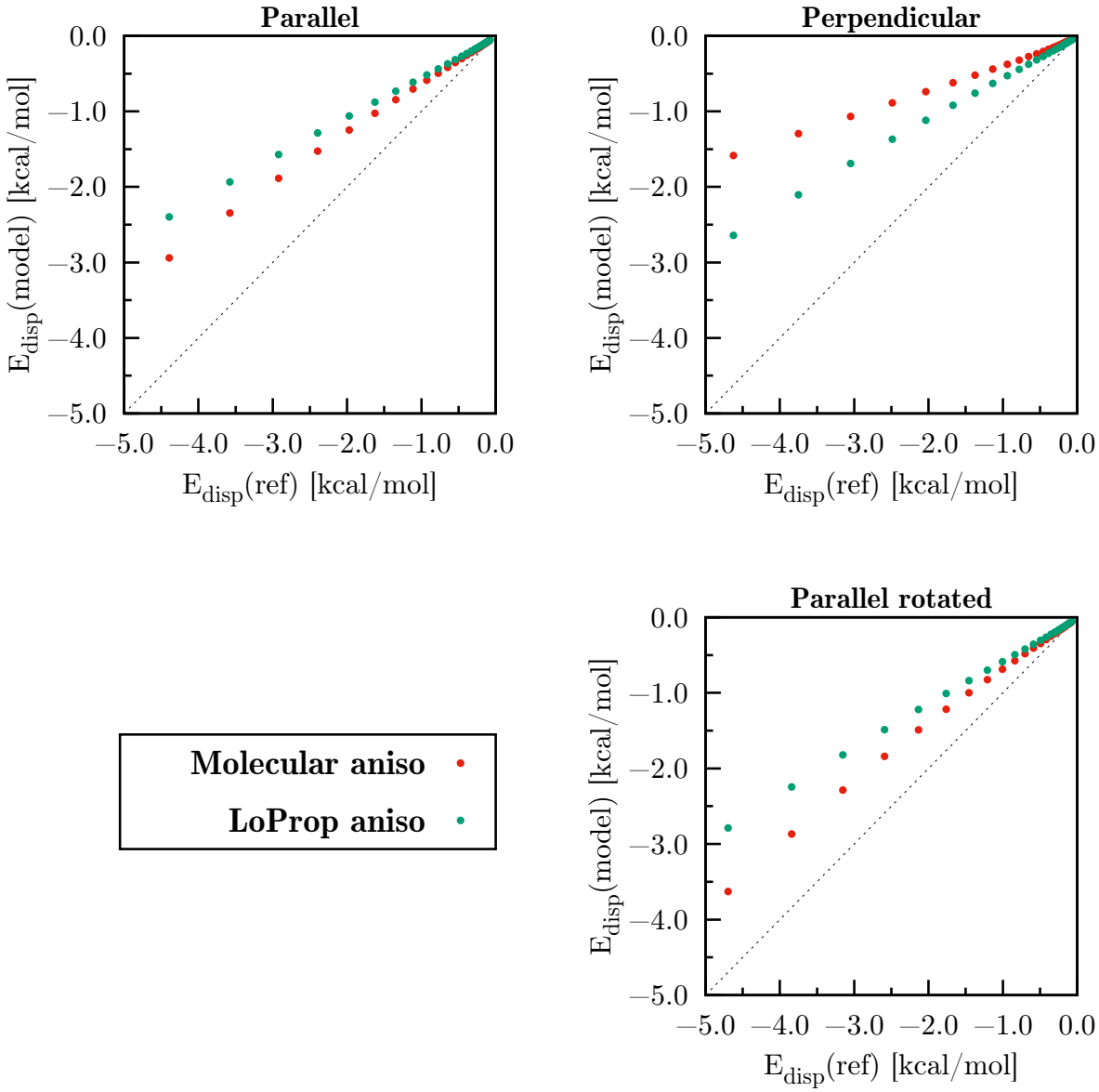

Figure S4: Scatter plots of the dispersion energy for the N_2–N_2 dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

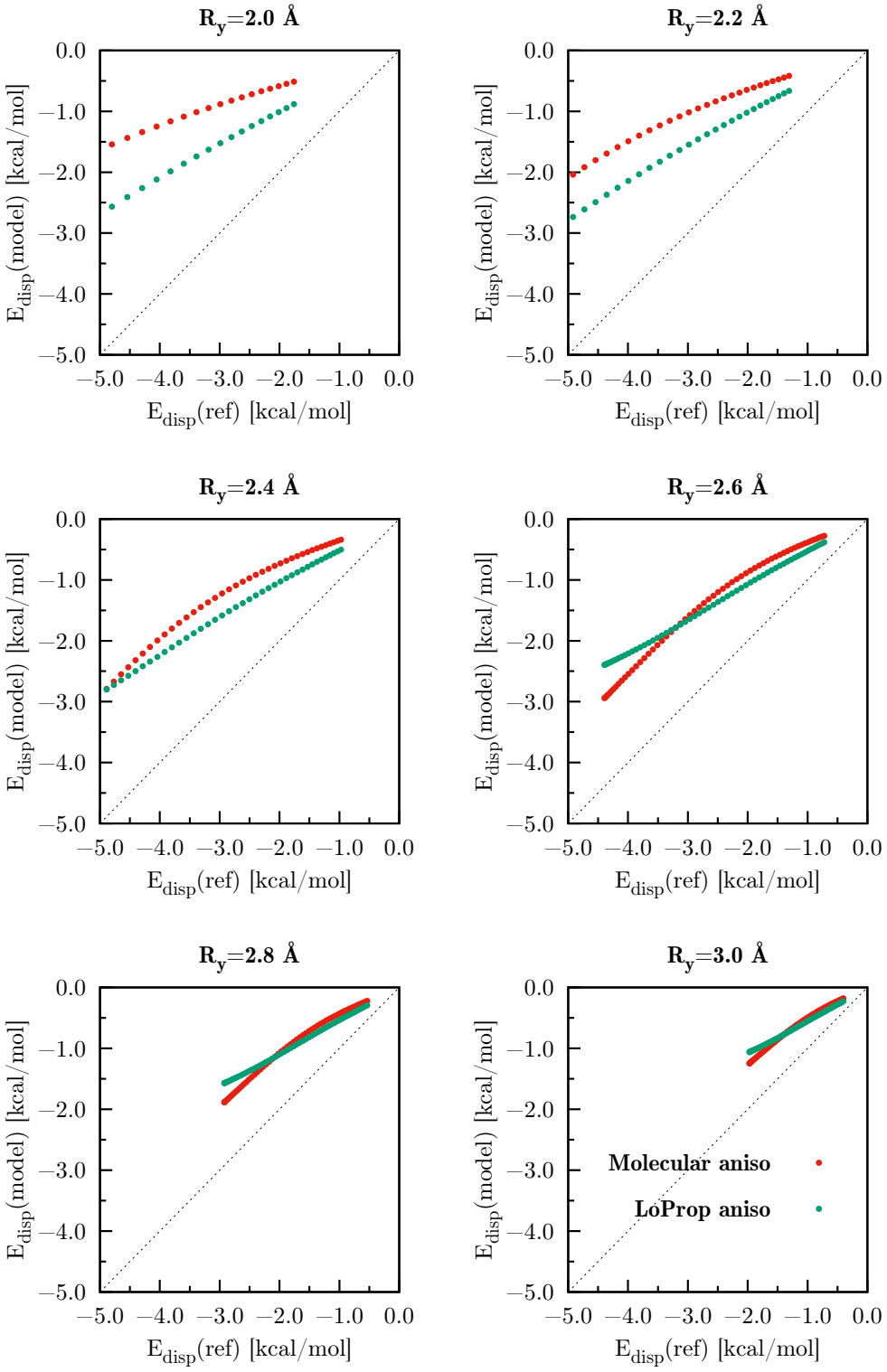

Figure S5: Scatter plots of the dispersion energy for the N_2–N_2 dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

3.3 CO dimer

Table S6: Reference structure in Cartesian coordinates (Å). Bond length was taken from experiment.

C	0.00000	0.00000	-0.56400
O	0.00000	0.00000	0.56400

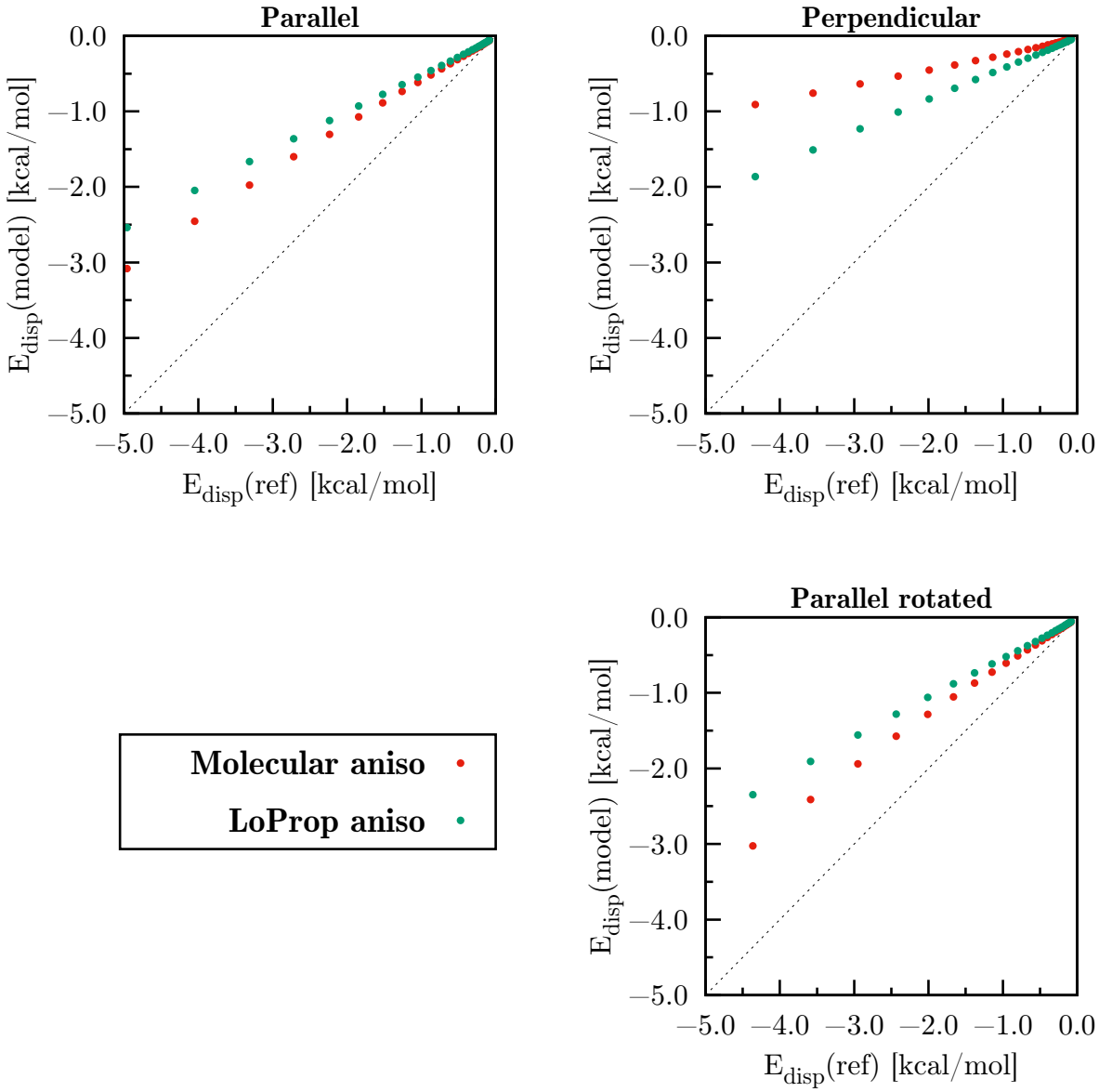

Figure S6: Scatter plots of the dispersion energy for the CO–CO dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

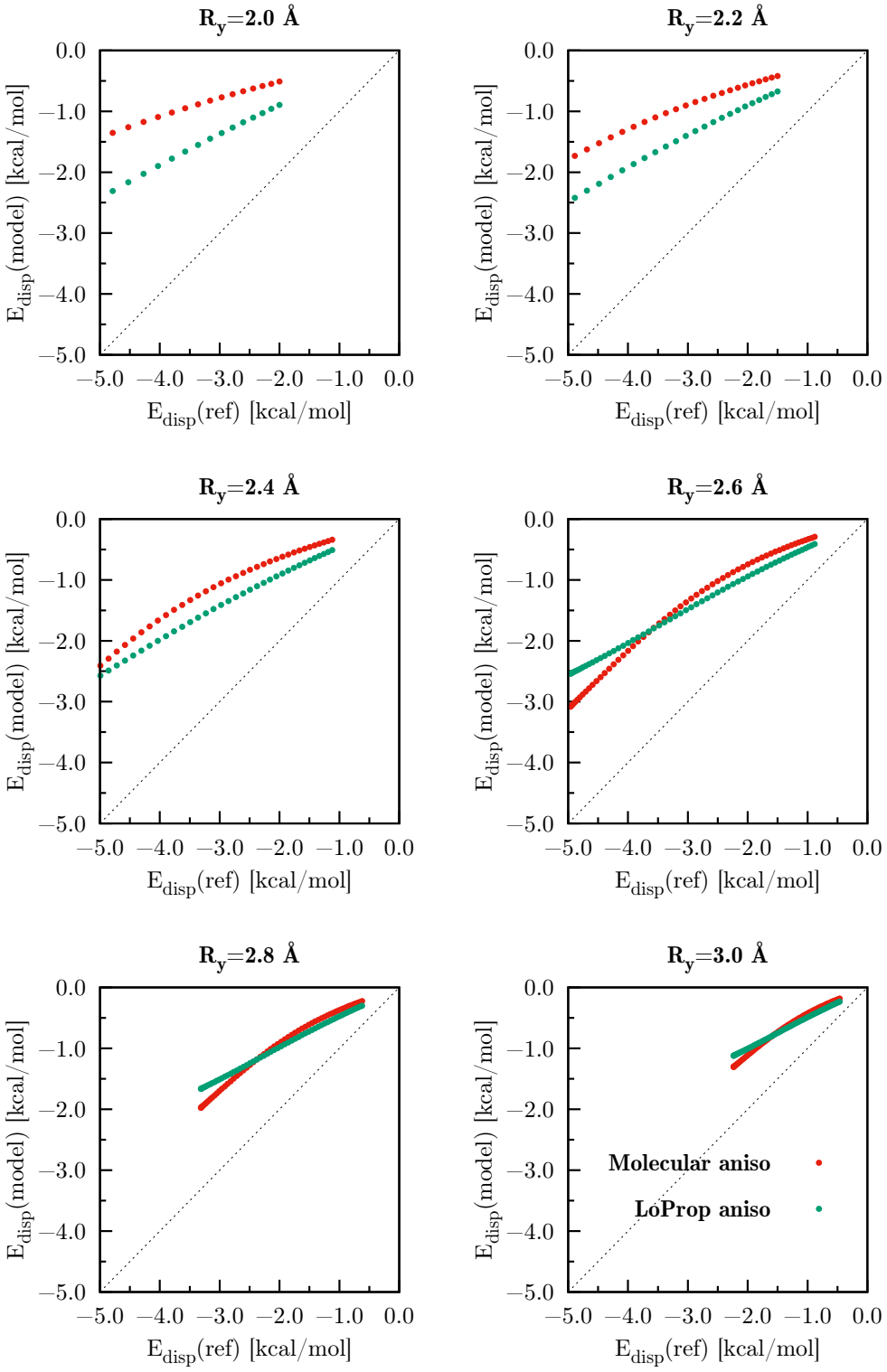

Figure S7: Scatter plots of the dispersion energy for the CO–CO dimers calculated with the anisotropic molecular and LoProp models versus the reference dispersion energy obtained with SAPT2+/aug-cc-pVTZ.

4 Benzene dimer

Table S7: Cartesian coordinates (in Å) for benzene optimized at the B3LYP/6-31++G** level

H	-0.896118	0.000000	-0.517374
H	1.255737	0.000000	-1.759748
H	3.407591	0.000000	-0.517374
H	3.407591	0.000000	1.967374
H	1.255737	0.000000	3.209748
H	-0.896118	0.000000	1.967374
C	0.044748	0.000000	0.025835
C	0.044748	0.000000	1.424165
C	1.255737	0.000000	-0.673330
C	1.255737	0.000000	2.123330
C	2.466726	0.000000	0.025835
C	2.466726	0.000000	1.424165

5 Methane dimer

Table S8: Cartesian coordinates (in Å) for methane optimized at the B3LYP/6-31++G** level

H	-0.000017	0.000031	1.092768
C	0.000030	-0.000009	-0.000034
H	-0.555621	0.867583	-0.364388
H	1.029263	0.047391	-0.364261
H	-0.473465	-0.915066	-0.364315

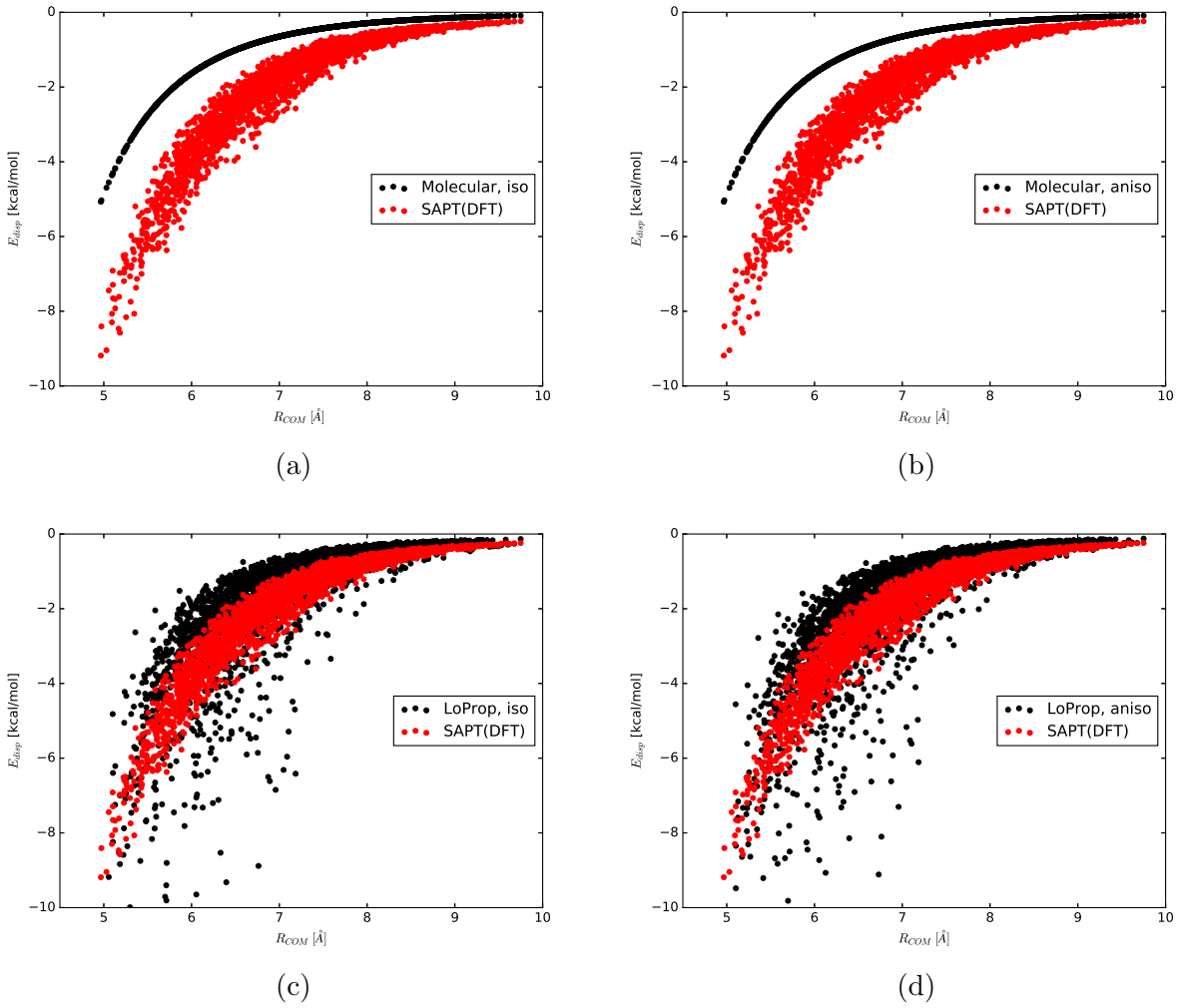

Figure S8: Molecular isotropic (a), molecular anisotropic (b), LoProp isotropic (c) and LoProp anisotropic (d) dispersion interaction energies for the CH_4–CH_4 dimer as a function of monomer distances.

6 Pyridine dimer

Table S9: Cartesian coordinates (in Å) for pyridine optimized at the B3LYP/6-31++G**

C	1.140650	-0.091634	2.099570
C	1.195938	-0.096073	0.703044
C	-0.000013	0.000003	-0.010155
C	-1.195949	0.096076	0.703052
C	-1.140642	0.091633	2.099586
N	0.000003	-0.000001	2.797579
H	2.054050	-0.165010	2.686406
H	2.151605	-0.172845	0.193744
H	-0.000011	0.000003	-1.096501
H	-2.151628	0.172849	0.193773
H	-2.054043	0.165008	2.686423

References

(1) Parr, R. G.; Yang, W. T. *Density-Functional Theory Atoms Mol.*; 1989.

(2) Salam, A. *Molecular Quantum Electrodynamics*; John Wiley & Sons, Inc., 2009; pp 378–380.

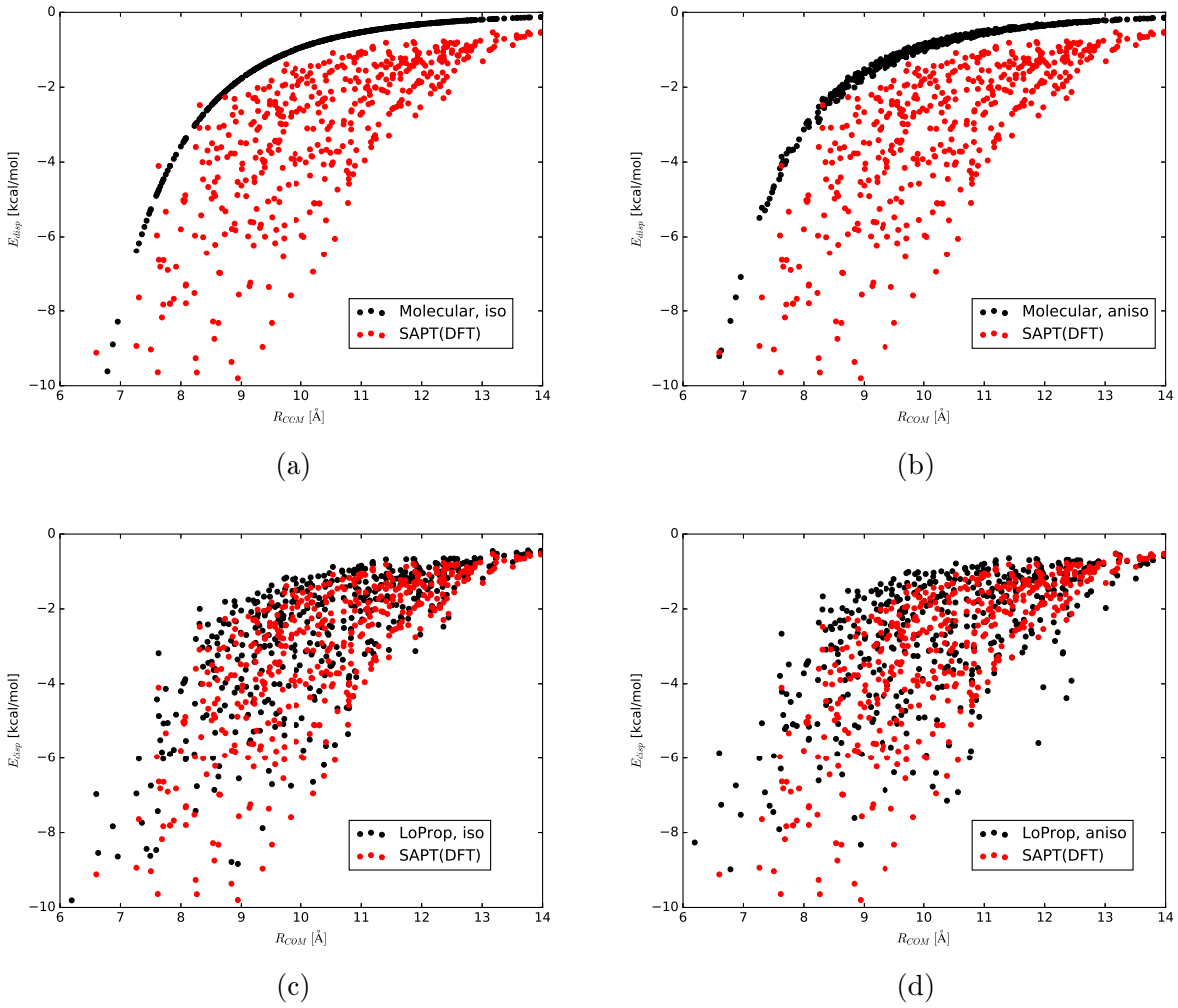

Figure S9: Molecular isotropic (a), molecular anisotropic (b), LoProp isotropic (c) and LoProp anisotropic (d) dispersion interaction energies for the pyridine–pyridine dimer as a function of monomer distances.