Electronic Supplementary Information for

$(4,4')$-Bipyridine in vacuo and in solvents: A quantum chemical study of a prototypical floppy molecule from a molecular transport perspective

Ioan Bâldea,[*a‡] **Horst Köppel,**[a] **and Wolfgang Wenzel**[b]

Impact of the basis sets on the bond metric data and vibrational frequencies

As support for the discussion in the main text on the impact of the basis sets, we present in Tables S1 and S2 bond metric data computed with various basis sets for the neutral and anionic species of 44BPY, respectively, and in Table S3 the frequencies of the Raman active modes of the anion.

Adiabatic energy surfaces

Besides the one-dimensional studies yielding the adiabatic curves $E_{A,N}(Q_f)$ and $E_{A,N}(Q_{8a})$ presented in the main text, we have also performed calculations of the two-dimensional adiabatic ground state energy surfaces $E_{N,A}(Q_f, Q_{8a})$ in sufficiently broad ranges $(-2 < Q_f < 4, -1 < Q_{8a} < 2)$, around the locations of the neutral's and anion's minima [at $Q_f = Q_{8a} = 0$ and $Q_f \simeq 2.73$, $Q_{8a} \simeq 0.84$, respectively]. For 44BPY in vacuo, the results can be fitted with the following polynomial expressions

$$
\begin{aligned}
E_N(Q_f, Q_{8a}) &= \mathcal{N}_0(Q_{8a}) + 101.8 f_h Q_{8a}^2 \\
&+ 3.8 \mathcal{N}_2(Q_{8a}) \left[Q_f - \overline{Q}_f^N(Q_{8a})\right]^2 \quad \text{(S1)} \\
&+ \mathcal{N}_4(Q_{8a}) \left[Q_f - \overline{Q}_f^N(Q_{8a})\right]^4,
\end{aligned}
$$

where

$$
\begin{aligned}
\mathcal{N}_0(Q_{8a}) &= -0.169 Q_{8a} - 0.417 Q_{8a}^2 + 1.760 Q_{8a}^3, \\
\mathcal{N}_2(Q_{8a}) &= 1.0168 + 0.8245 Q_{8a} - 0.0635 Q_{8a}^2, \\
\mathcal{N}_4(Q_{8a}) &= 0.825, \quad \text{(S2)} \\
\overline{Q}_f^N(Q_{8a}) &= 0.024 Q_{8a} - 0.030 Q_{8a}^2 + 0.025 Q_{8a}^3 + 0.0057 Q_{8a}^4,
\end{aligned}
$$

[a] *Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany.*

[‡] E-mail: ioan@pci.uni-heidelberg.de. Also at National Institute for Lasers, Plasmas, and Radiation Physics, ISS, Bucharest, Romania

[b] *Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), D-76131 Karlsruhe, Germany*

and

$$
\begin{aligned}
E_A(Q_f, Q_{8a}) &= \mathcal{A}_1(Q_{8a}) + \mathcal{A}_2(Q_{8a}) \left[Q_f - \overline{Q}_f^A(Q_{8a})\right]^2 \\
&+ \mathcal{A}_3(Q_{8a}) \left[Q_f - \overline{Q}_f^A(Q_{8a})\right]^3 \quad \text{(S3)} \\
&+ \mathcal{A}_4(Q_{8a}) \left[Q_f - \overline{Q}_f^A(Q_{8a})\right]^4
\end{aligned}
$$

where

$$
\begin{aligned}
\mathcal{A}_1(Q_{8a}) &= -603.4 - 165.6 Q_{8a} + 99.0 f_h Q_{8a}^2, \\
\mathcal{A}_2(Q_{8a}) &= 40.0 f_f - 3.5 Q_{8a} + 4.5 Q_{8a}^2, \\
\mathcal{A}_3(Q_{8a}) &= 9.510 - 0.988 Q_{8a} + 0.007 Q_{8a}^2, \\
\mathcal{A}_4(Q_{8a}) &= 0.7782, \quad \text{(S4)} \\
\overline{Q}_f^A(Q_{8a}) &= 2.8677 - 0.1740 Q_{8a} + 0.0132 Q_{8a}^2.
\end{aligned}
$$

Above, all energies are expressed in meV, and the reason of introducing the factors $f_h = 1$ and $f_f = 1$ will become clear below.

The fact that a harmonic treatment is not sufficiently accurate for large amplitude motion in molecules with a floppy degree of freedom is well known[11]. Notice that the anharmonicity related to this degree of freedom manifests itself not only in the higher-order powers of Q_f but also in cross anharmonic terms (like $Q_{8a}Q_f^2$ and higher). Essentially, the differences between the values of $\lambda_{N,A}$ and the sums $\lambda_{N,A}^{8a} + \lambda_{N,A}^f$ represent the contribution of the other in-plane modes of A symmetry (point group D_2 of 44BPY^0): seven Raman active modes (i. e., excluding the mode 8a from the modes listed in Table S3) and two C-H stretching modes. The latter are not important not only because of their very small reorganization energies obtained by these calculations but also due to their high frequencies $\sim 3150\,\text{cm}^{-1} = 0.39\,\text{eV}$ and $\sim 3191\,\text{cm}^{-1} = 0.40\,\text{eV}$, that is, larger than the highest Γ-values of the level widths characterizing molecular devices. In general, fast modes, of (high) frequencies ω_ν (comparable to or higher than Γ) negligibly contribute to reorganization.

Considered alone, each of the aforementioned seven modes with small individual contributions to reorganization exhibits a harmonic behavior. It has been argued[12] that the effect of

Geom.	Expt.	6-31g(+*)^c	6-31+g(d)	cc-pVDZ	cc-pVTZ (^{d})	aug-cc-pVDZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
C_1C_2	1.470^b	1.484	1.485	1.485	1.480 (1.480)	1.484	1.480	1.480	1.481
C_1C_3	1.3916 ± 0.0004^a	1.406	1.403	1.404	1.396 (1.397)	1.404	1.396	1.396	1.396
C_3C_5	1.3938 ± 0.0006^a	1.396	1.396	1.396	1.388 (1.389)	1.395	1.388	1.388	1.388
C_5N_7	1.3376 ± 0.0004^a	1.347	1.340	1.340	1.333 (1.333)	1.340	1.333	1.333	1.333
C_3H_{13}	1.0826 ± 0.0004^a	1.084	1.086	1.092	1.081 (1.081)	1.090	1.081	1.081	1.081
C_5H_{15}	1.0865 ± 0.0004^a	1.086	1.088	1.095	1.084 (1.084)	1.093	1.084	1.084	1.084
$C_2C_1C_3$	—	121.6	121.6	121.6	121.6 (121.6)	121.6	121.6	121.6	121.6
$C_1C_3C_5$	118.53 ± 0.03^a	119.4	119.3	119.3	119.4 (119.4)	119.3	119.4	119.4	119.4
$C_3C_5N_7$	123.80 ± 0.03^a	123.9	123.9	124.1	123.8 (123.8)	123.9	123.7	123.7	123.7
$C_5N_7C_9$	116.94 ± 0.03^a	116.5	116.8	116.4	116.9 (116.9)	116.8	116.9	117.0	117.0
$C_1C_3H_{13}$	121.36 ± 0.04^a	120.8	120.9	120.8	120.8 (120.8)	120.9	120.8	120.8	120.8
$C_3C_5H_{15}$	120.19 ± 0.03^a	119.9	120.1	119.9	120.0 (120.0)	112.0	120.0	120.0	120.0
$C_3C_1C_{11}$	118.40 ± 0.03^a	116.9	116.9	116.7	116.8 (116.8)	116.8	116.9	116.9	116.9
θ_{eq}	37.2^b	35.2	38.0	36.4	36.8 (36.9)	37.3	37.0	37.1	37.3

Table S1 The optimized geometry of the neutral 44BPY molecule computed by DFT/B3LYP and various basis sets indicated in the table. Notice that the increase in the basis sets does not further improve the agreement with experimental data (^{a} — values for pyridine, Ref. [1]; ^{b} — Ref. [2]; ^{c} — Ref. [3]; ^{d} — values given in parenthesis in this column are from Ref. [4]). The atom numbering is given in Fig. 1 of the main text. See the main text for details.

Geometry	6-31 g(+*)$^{a 5}$	6-31+g(d)	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
C_1C_2	1.435	1.434	1.435	1.427	1.435	1.428	1.428	1.428
C_1C_3	1.439	1.436	1.437	1.431	1.437	1.430	1.431	1.430
C_3C_5	1.383	1.384	1.385	1.375	1.385	1.376	1.375	1.376
C_5N_7	1.367	1.357	1.358	1.352	1.358	1.351	1.351	1.351
C_3H_{13}	1.086	1.087	1.090	1.082	1.090	1.081	1.081	1.081
C_5H_{15}	1.090	1.092	1.096	1.088	1.096	1.087	1.087	1.087
$C_2C_1C_3$	123.5	123.5	123.5	123.6	123.5	123.5	123.6	123.5
$C_1C_3C_5$	121.1	121.0	121.0	121.1	121.0	121.0	121.0	121.0
$C_3C_5N_7$	125.7	125.6	125.6	125.7	125.6	125.5	125.6	125.4
$C_5N_7C_9$	113.4	113.8	113.9	113.7	113.9	114.0	113.9	114.1
$C_1C_3H_{13}$	120.4	120.7	120.8	120.7	120.8	120.8	120.7	120.8
$C_3C_5H_{15}$	119.3	119.1	118.9	118.9	118.9	119.0	118.9	119.0
$C_3C_1C_{11}$	113.0	113.0	113.0	112.8	113.0	113.0	112.9	113.0

Table S2 Results for the anion 44BPY$^{\bullet-}$ (found to be planar, i. e., $\theta = C_3\widehat{C_1C_2}C_4 = 0$) obtained at the DFT/B3LYP level and various basis sets. ^{a} Ref. [3]. See the main text for details.

Mode	expt.	6-31g(+*)[5]	6-31+g(d)	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVDZ (acetonitrile)
ring i. p. def. (6a)	—	330.6	324.3	323.0	324.4	324.3	321.9	322.4
ring breath (1)	740	759.3	747.9	748.5	750.0	748.6	748.7	748.6
ring i. p. def. (12) ring stretch +	985	1006.9	999.5	997.9	999.7	1000.3	992.2	992.9
ring i. p. def. (18a)	1042	1071.2	1075.0	1066.6	1069.1	1069.4	1062.3	1057.3
CH i. p. bend (9a)	1230	1309.8	1310.0	1299.6	1286.8	1286.9	1297.4	1294.9
inter-ring stretch (13; Ω) CH i. p. bend +	1351	1391.4	1371.3	1366.5	1367.9	1365.5	1361.2	1363.7
ring stretch (19a)	1506	1548.4	1538.3	1529.4	1528.4	1527.3	1521.1	1523.7
ring stretch (8a)	1611	1670.2	1649.2	1663.9	1648.5	1643.2	1640.5	1646.5
empirical scaling factor f_{sc}	—	0.968	0.975	0.977	0.979	0.980	0.982	0.982

Table S3 Frequencies of the relevant Raman active modes of the radical anion 44BPY[•−] computed by using DFT/B3LYP and various basis sets. Mode assignment (in parentheses) derived from Wilson's notation[6–8] adapted by Varsanyi[9] for monosubstituted benzenes ([a] experimental values from Ref.[10]). See the main text for details.

multiple harmonic modes can be replaced by a single effective harmonic mode. Adapted to the present situation, one can consider that these seven modes renormalize the frequency of mode 8a, and this can be accounted for by the factor $f_h < 1$ ($\omega_{8a} \rightarrow \tilde{\omega}_h = f_h \omega_{8a}$), which is consistent with the fact that their frequencies ω_μ are substantially lower than ω_{8a}; see the values in Table S3. The reorganization energies $\lambda_N \simeq 0.23\,\mathrm{eV}$ and $\lambda_A \simeq 0.35\,\mathrm{eV}$ can be reproduced by choosing $f_h \simeq 0.5$ and $f_f \simeq 1.14$.

References

1 F. Mata, M. J. Quintana and G. O. Sorensen, *J. Mol. Struct.*, 1977, **42**, 1 – 5.

2 A. Almenningen and O. Bastiansen, *Skr. K. Nor. Vidensk. Selsk.*, 1958, **4**, 1.

3 M. Castellà-Ventura and E. Kassab, *J. Raman Spectr.*, 1998, **29**, 511–536.

4 Ángel J. Pérez-Jiménez, J. C. Sancho-García and J. M. Pérez-Jordá, *J. Chem. Phys.*, 2005, **123**, 134309.

5 The notation "(+*)" means that diffuse and polarization functions have been added only to the nitrogen atoms.

6 H. Kihara and Y. Gondo, *J. Raman Spectrosc.*, 1986, **17**, 263–267.

7 O. Poizat, G. Buntinx, M. Ventura and M. F. Lautie, *J. Phys. Chem.*, 1991, **95**, 1245–1253.

8 G. Buntinx, P. Valat, V. Wintgens and O. Poizat, *J. Phys. Chem.*, 1991, **95**, 9347–9352.

9 G. Varsanyi, *Assignments for Vibrational Spectra of Benzene Derivatives*, Adam Hilger, London, 1974, vol. 1.

10 L. Ould-Moussa, O. Poizat, M. Castellà-Ventura, G. Buntinx and E. Kassab, *J. Phys. Chem.*, 1996, **100**, 2072–2082.

11 M. J. Bramley and T. Carrington Jr., *J. Chem. Phys.*, 1994, **101**, 8494–8507.

12 W. Schmickler, *Electrochimica Acta*, 1996, **41**, 2329 – 2338.