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Electronic Supporting Information For: Accurate & Cheap Calculations of the Lowest Triplet State Energy: An Experimentalist's Guide[†]

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1 Vertical transitions

Most of the experimentally measured quantities presented in the main text and 1 were measured using optical spectroscopy so the values represent vertical transitions. Moreover, the previous work of Parac and Grimme presented the calculated vertical absorption transitions.⁷ As such, the vertical energies were calculated (while ignoring the ZPE) using the optimized ground singlet or triplet geometries, and the results are shown in Figure 1. Given the failure of this approach to accurately predict transitions between molecular orbitals with non-bonding character or Jahn-Teller activity, we only present the results of unmixed $^1\pi\pi - ^3\pi\pi^*$ transitions in Jahn-Teller inactive systems. We can clearly see that the Stoke's shifts of these transitions are greatly overestimated however, excellent correlations between experiment and theory are still achieved. The Pearson's r values of calculations of E_{aT1} using B3LYP/3-21G and TDDFT B3LYP/cc-pVTZ are respectively 0.9966 and 0.9793, showing that a time-independent calculation with a smaller basis set provides a better correlation between calculation and experiment for this homologous series.

References

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Table 1 Experimental and calculated first excited triplet state energies, E_{T1} , of extended π systems in eV using B3LYP/3-21G. The predicted values are calculated using the parameters in Table 2 in the main text. Standard errors are given in parentheses.

No.	$E_{T,exp}^a$	$E_{T,calc}$	E_{pred}	ΔE
23	1.56	1.66	1.53(4)	-0.03
24	1.19(2) ^b	1.35	1.26(4)	0.07
24 ^e	-	1.37	1.28(4)	
25	1.68 ^c	1.84	1.69(4)	0.01
25 ^e	-	1.85	1.70(4)	
26	1.79 ^c	1.99	1.82(4)	0.03
26 ^e	-	2.00	1.83(4)	
27	1.41 ^d	1.55	1.43(4)	0.02
28	3.05 ^f	3.38	3.03(5)	-0.02
29	1.95	2.07	1.89(4)	-0.06
30	1.93	2.05	1.87(4)	-0.06
31	2.68	2.96	2.67(5)	-0.01
32	2.63	2.89	2.61(5)	-0.02
33	2.64	2.71	2.45(5)	-0.19
34	1.86(5) ^g	1.85	1.69(4)	-0.22
35	1.86(5) ^g	1.90	1.74(4)	-0.17
36	1.86(5) ^g	1.75	1.61(4)	-0.30

^a Values taken from Table 2 in Ref. 1 unless otherwise stated.

^b Value taken from sensitized triplet energy transfer experiments in Ref. 2.

^c Value taken from phosphorescence measurements in Ref. 3.

^d Value taken from Ref. 4.

^e Using a simplified molecule with higher symmetry, where R=H (see Fig. 3 in the main text).

^f Value taken from optically detected magnetic resonance phosphorescence spectra.⁵

^g Value taken from phosphorescence measurements.⁶

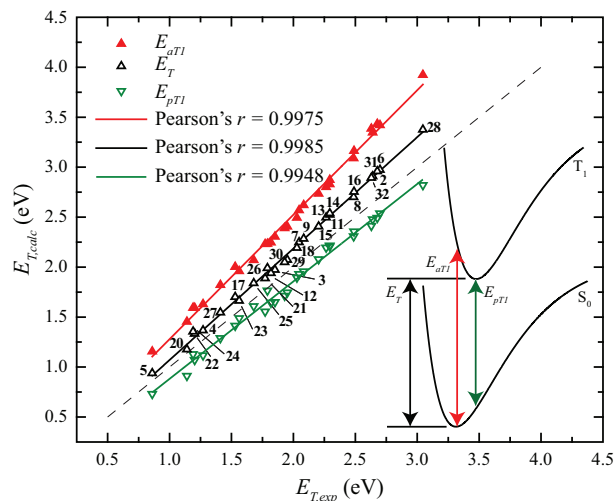


Fig. 1 The calculated vertical transition energies for E_T using R(O)B3LYP/3-21G as a function of experimental results.

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2 Step-by-step Guide

1. Optimize the geometry of the S_0 state using B3LYP/3-21G
2. Optimize the geometry of the T_1 state using B3LYP/3-21G
3. Find the TOTAL ENERGY of the optimized geometry and subtract the S_0 energy from the T_1 energy. Convert the units of this result from Hartrees to eV to yield E_{calc} .
4. Apply the following empirical correction to find your predicted value (from the last line of Table 2 of the main text):

$$E_{pred} = (E_{calc} + 0.04) / 1.12$$

An example for tetracene is provided below. Note that D_{2h} symmetry is used in this particular example.

2.1 Example S₀ Geometry Optimization

! Minimize (Energy/Geometry) B3LYP/3-21G

```
$CONTRL
COORD=UNIQUE
ICHARG=0
MAXIT=200
MULT=1
RUNTYP=OPTIMIZE
SCFTYP=RHF
UNITS=ANGS
DFTTYP=B3LYP
$END
$BASIS
GBASIS=N21
NGAUSS=3
$END
$STATPT
NSTEP=200
$END
$SYSTEM
MWORDS=80
$END
$DATA
Tetracene
DNH 2
```

```
C 6.0 0.0000000000 0.7843120000 -0.0000000000
C 6.0 2.3533530000 0.7160330000 -0.0000000000
C 6.0 1.2004900000 1.4085480000 -0.0000000000
H 1.0 1.2339770000 2.5111720000 -0.0000000000
C 6.0 4.6875070000 0.6440280000 -0.0000000000
C 6.0 3.5434530000 1.3443800000 -0.0000000000
H 1.0 5.6584380000 1.1670260000 -0.0000000000
H 1.0 3.6028760000 2.4455270000 -0.0000000000
$END
```

2.2 Example T₁ Geometry Optimization

! Minimize (Energy/Geometry) B3LYP/3-21G

```
$CONTRL
COORD=UNIQUE
ICHARG=0
MAXIT=200
MULT=3
RUNTYP=OPTIMIZE
SCFTYP=ROHF
UNITS=ANGS
DFTTYP=B3LYP
$END
$BASIS
GBASIS=N21
NGAUSS=3
$END
$STATPT
NSTEP=200
```

\$END
\$SYSTEM
MWORDS=80
\$END
\$DATA
Tetracene
DNH 2

C 6.0 0.0000000000 0.7843120000 -0.0000000000
C 6.0 2.3533530000 0.7160330000 -0.0000000000
C 6.0 1.2004900000 1.4085480000 -0.0000000000
H 1.0 1.2339770000 2.5111720000 -0.0000000000
C 6.0 4.6875070000 0.6440280000 -0.0000000000
C 6.0 3.5434530000 1.3443800000 -0.0000000000
H 1.0 5.6584380000 1.1670260000 -0.0000000000
H 1.0 3.6028760000 2.4455270000 -0.0000000000
\$END

2.3 Calculation output and prediction

Find the last instance of "TOTAL ENERGY" in the output files. The S_0 output is below.

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -3136.4529842180
TWO ELECTRON ENERGY = 1335.3169141648
NUCLEAR REPULSION ENERGY = 1112.2315396678

TOTAL ENERGY = -688.9045303854

ELECTRON-ELECTRON POTENTIAL ENERGY = 1335.3169141648
NUCLEUS-ELECTRON POTENTIAL ENERGY = -3819.8425121722
NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1112.2315396678

TOTAL POTENTIAL ENERGY = -1372.2940583396
TOTAL KINETIC ENERGY = 683.3895279542
VIRIAL RATIO (V/T) = 2.0080700716

The T_1 output is below.

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -3131.9514155904
TWO ELECTRON ENERGY = 1333.0884396988
NUCLEAR REPULSION ENERGY = 1110.0086959230

TOTAL ENERGY = -688.8542799685

ELECTRON-ELECTRON POTENTIAL ENERGY = 1333.0884396988

NUCLEUS-ELECTRON POTENTIAL ENERGY = -3815.3056570065

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1110.0086959230

TOTAL POTENTIAL ENERGY = -1372.2085213847

TOTAL KINETIC ENERGY = 683.3542414161

VIRIAL RATIO (V/T) = 2.0080485906

The value of E_{calc} is $(-688.8542799685 - -688.9045303854) \times 27.2114 = 1.367$ eV. Now, we apply the empirical correction to arrive at $E_{pred} = (1.367 + 0.04)/1.12 = 1.25$ eV, in excellent agreement with the measured value for tetracene.