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# Supplementary Information to:

# The Electronic Structure of Pyracene: A Spectroscopic and Computational Study

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**This material contains:**

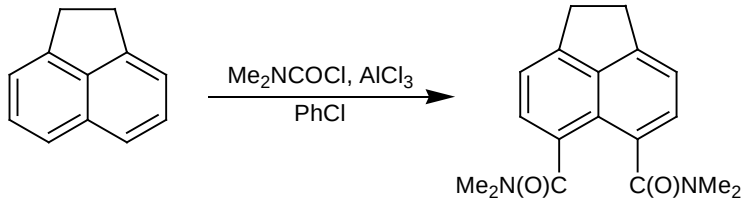
# A) The Synthesis of Pyracene: Experimental Details

## 1. General Experimental Procedure

All chemicals were used as received without further purification unless otherwise stated. Reactions requiring anhydrous conditions were performed in dried glassware under an atmosphere of dry nitrogen. Water free solvents were dried and distilled prior to use according to standard protocols. Reaction progress was monitored by thin-layer chromatography (TLC) on Merck pre-coated plates (TLC silica gel 60 $F_{254}$, 0.20 mm). Flash column chromatography was performed on silica gel (particle size: 0.04-0.063 mm) purchased from Merck with indicated solvents (v/v) using columns with aligned length and diameter. $^{1}$H- and $^{13}$C-NMR were recorded on Bruker AVANCE 400 FT-NMR- (400 MHz) spectrometer. Chemical shifts are referenced relative to internal chloroform ($CDCl_3$: $^{1}$H, δ=7.26; 13C, δ=77.16), dichloromethane ($CD_2Cl_2$: $^{1}$H, δ=5.32; $^{13}$C, δ=53.84) and dimethyl sulfoxide (DMSO: $^{1}$H, δ=2.50; $^{13}$C, δ=39.52) in ppm, respectively. Coupling patterns are assigned as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet) (or combinations) and coupling constants are reported in Hz. Fusion points (Fp.) were determined by using a Reichert Austria Kofler instrument and are uncorrected. Infrared (IR) spectra were recorded on a Jasco FT-IR-430 spectrometer using an ATR unit. Absorptions are reported in $cm^{-1}$ and noted as following: vs (very strong), s (strong), m (medium), w (weak), br. (broad). Electron impact (EI) mass spectrometry was performed on a Finnigan MAT 90 or Varian MS 320.

## 2. Experimental Procedure and Characterisation

Synthesis of N,N,N´,N´-Tetramethylacenaphthene-5,6-dicarboxamide **3:**



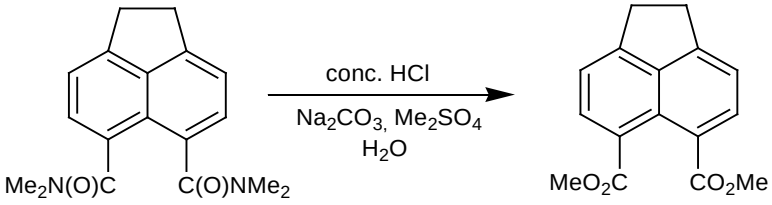

A solution of 20.0 g (130 mmol) acenapthene in 100 ml dry chlorbenzene was cooled in nitrogen atmosphere to 0 °C and 32.0 ml dimethylcarbamoyl chloride was added at once. Within 5 min 48.0 g (360 mmol) aluminium chloride were added and the reaction mixture was heated to 80 °C for 3 h. After cooling to 0 °C another portion of 14.0 ml (150 mmol) dimethylcarbamoyl chloride and 28.8 g (220 mmol) aluminium chloride were added and the solution was refluxed for 2.5 h. The black reaction mixture was cooled to rt and carefully poured into 600 ml of 5 % aqueous hydrochloric acid precooled to 0 °C. The solution was extracted with chloroform (3×200 ml) the organic layer was washed with water (2×100 ml) and saturated aqueous $NaHCO_3$ solution (100 ml). After drying over $MgSO_4$ and removal of the solvent in vacuum, the crude solid was purified by recrystallization from ethanol-water (20 ml/32 ml) to afford 21.9 g (57 %) of **3** as a pale brown solid.

**Fp**. 112-120 °C

**$^{1}$H-NMR** (400 MHz, [$d_6$]-DMSO): δ = 7.35 (d, 2H, $^{3}J$ = 7.20 Hz, C$H_{arom.}$), 7.33 (d, 2H, $^{3}J$ = 8.40 Hz, C$H_{arom.}$), 3.39 (s, 4H, C$H_2$), 2.93 (s, 3H, C$H_3$), 2.74 (s, 3H, C$H_3$) ppm.

**$^{13}$C-NMR** (100 MHz, [$d_6$]-DMSO): δ = 147.1 (*C*O), 139.0 ($C_q$), 129.9 ($C_q$), 127.1 ($C_q$), 124.6 ($C_t$H), 119.2 ($C_t$H), 38.7 ($C_p$H$_3$), 34.3 (*C*#H$_3$), 29.7 ($C_s$H$_2$) ppm.
**FT-IR** (ATR): $\tilde{\nu}$= 3420 (br. w), 2931 (w), 1623 (s), 1507 (m), 1486 (m), 1387 (s), 1176 (m), 1100 (m), 846 (s), 640 (m) cm$^{-1}$.
**MS** (EI, 70 eV): m/z (%) = 319.1 ([M + Na$^+$], 100), 281.1 ([M$^+$ - CH$_3$]).

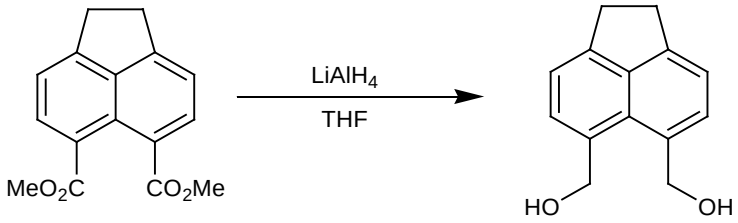
Synthesis of Dimethyl acenaphthene-5,6-dicarboxylate **4**:




A suspension of 12.4 g (420 mmol) **3** (5.86 g, 19.8 mmol) in 100 ml of concentrated hydrochloric acid was refluxed for 2h. After cooling to 0 °C, the brown solid was filtered and washed with water. The solid was taken up with 430 ml of hot 2N aqueous sodium hydroxide solution and the insoluble material was filtered off. The filtrate was cooled to 0 °C and acidified with concentrated hydrochloric acid. The resulting white solid was filtered and washed with water. The acenaphthene dicarboxylic acid was dissolved in a solution of 6.82 g (64.3 mmol) $Na_2CO_3$ in 100 ml water by heating at 60 °C. 8.48 ml (89.4 mmol) dimethyl sulfate was added and heating was continued for 45 min before another portion of 12.7 ml (134 mmol) dimethyl sulfate and 6.65 g (62.7 mmol) $Na_2CO_3$ were added and stirred at 60 °C for 75 min. After cooling to rt, the resulting solid was filtered, washed with water and purified by recrystallization from dioxane (30 ml) to afford 5.25 g (46 %) of **4** as a colourless solid.

**Fp.** 175-178 °C
**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.97 (d, 2H, $^3J$ = 7.60 Hz, C$H_{arom.}$), 7.33 (d, 2H, $^3J$ = 7.20 Hz, C$H_{arom.}$), 3.86 (s, 6H, C$H_3$), 3.40 (s, 4H, C$H_2$) ppm.
**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ = 169.4 (*C*O), 151.1 ($C_q$), 139.9 ($C_q$), 132.4 ($C_t$H), 125.7 ($C_q$), 119.4 ($C_t$H), 52.0 ($C_p$H$_3$), 30.5 ($C_s$H$_2$) ppm.
**FT-IR (ATR):** $\tilde{\nu}$= 2956 (w), 2319 (w), 1717 (vs), 1597 (m), 1441 (m), 1276 (s), 1213 (s), 1113 (s), 766 (s) cm$^{-1}$.
**MS** (EI, 70eV): m/z (%) = 293.1 ([M + Na$^+$], 10), 271.1 ([M + H$^+$], 3), 270.1 ([M$^+$], 100).

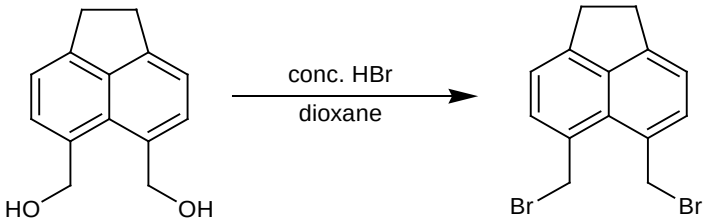
Synthesis of 5,6-Dihydroxymethylacenaphthene **5**:




A suspension of 1.50 g (39.5 mmol) $LiAlH_4$ in 150 ml of dry THF was precooled to 0 °C and 5.25 g (19.4 mmol) **4** were added in small portions. The reaction mixture was stirred at rt for 1 h and refluxed for 2 h. After cooling with an ice bath, the reaction was quenched by slowly adding a mixture of THF/$H_2O$ (60ml/30 ml). The resulting white solid was filtered, dried over $P_4O_{10}$ and recrystallized from 20 ml dioxane to afford 3.14 g (75 %) of **5** as colourless solid.

**Fp.** 213-215 °C
**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.50 (d, 2H, $^3J$ = 7.20 Hz, C$H_{arom.}$), 7.25 (d, 2H, $^3J$ = 7.20 Hz, C$H_{arom.}$), 5.18 (s, H, O*H*), 5.00 (s, 4H, C$H_2$OH), 3.32 (s, 4H, C$H_2$) ppm.
**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ = 145.6 ($C_q$), 134.4 ($C_q$), 129.4 ($C_q$), 118.8 ($C_q$), 63.1($C_pH_2$OH), 29.4 ($C_sH_2$) ppm.
**FT-IR (ATR):** $\tilde{\nu}$= 3340 (m), 3240 (br. M), 2921 (s), 2887 (s), 1604 (m), 1017 (s), 842 (s) cm$^{-1}$.
**MS** (EI, 70 eV): m/z (%) = 214.1 ([M$^+$], 28), 196.1 ([M$^+$ - $H_2O$], 100), 167.1 ([M$^+$ - $H_2O$, -$C_2H_5$], 65), 152.1 ([M$^+$ - $H_2O$, - $C_2H_5$, - $CH_3$], 38).

Synthesis of 5,6-Dihydroxymethylacenaphthene **6**:

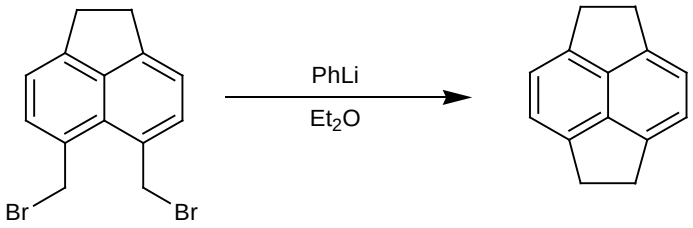



In a round bottom flask 3.14 g (14.7 mmol) of **5** were added at rt to a mixture of 15.7 ml hydro bromic acid (48 % in $H_2O$) and 32 ml of dioxane. The reaction was stirred for 3 h at rt while the white solid disappeared and a greenish precipitate formed. The solid was filtered off and recrystallized from 30 ml toluene to afford 3.98 g (80 %) of **6** as olive-green needles.

**Fp.** 158-162 °C
**$^1$H-NMR** (400 MHz, $CD_2Cl_2$): δ = 7.58 (d, 2H, $^3J$ = 7.20 Hz, C$H_{arom.}$), 7.30 (d, 2H, $^3J$ = 7.20 Hz, C$H_{arom.}$), 5.29 (s, 4H, C$H_2$Br), 3.36 (s, 4H, C$H_2$) ppm.
**$^{13}$C-NMR** (100 MHz, $CD_2Cl_2$): δ = 150.2 ($C_q$), 141.7 ($C_q$), 134.5 ($C_t$H), 129.9 ($C_q$), 127.7 ($C_q$), 120.5 ($C_t$H), 37.4 ($C_pH_2$Br), 30.7 ($C_sH_2$) ppm.
**FT-IR (ATR):** $\tilde{\nu}$= 2916 (s), 2829 (s), 1596 (m), 1191 (s), 843 (s), 653 (s) cm$^{-1}$.

**MS** (EI, 70 eV): m/z (%) = 341.9 ([$M^+$ $C_{14}H_{12}{}^{81}Br^{81}Br$], 6), 339.9 ([$M^+$ $C_{14}H_{12}{}^{81}Br^{79}Br$], 13), 337.9 ([$M^+$ $C_{14}H_{12}{}^{79}Br^{79}Br$], 259.0 ([$M^+$ - $^{81}Br$], 100), 180.1 ([$M^+$ - 2 $^{79}Br$], 66), 179.1 ([$M^+$ -$^{81}Br$, - $H^{79}Br$], 90), 178 ([$M^+$ - $H^{81}Br$,- $H^{81}Br$, 41), 149.1 ([$M^+$ - $^{81}Br$,- $H^{79}Br$, - $C_2H_6$], 60), 82.0 ([$H^{81}Br$], 45), 80.0 ([$H^{79}Br$], 46), 79.0 ([$^{79}Br$], 29).

Synthesis of Pyracene **1**:

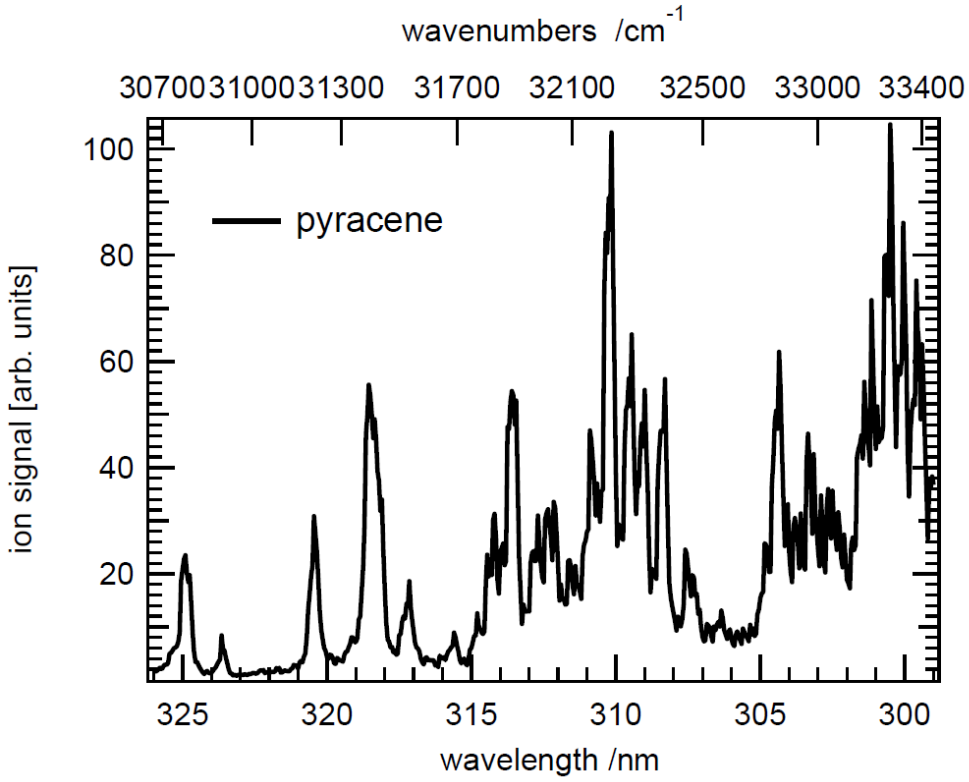



1.00 g (2.94 mmol) of **6** was placed in 50 ml of dry $Et_2O$ in a Schlenk tube under nitrogen atmosphere. 1.93 ml (3.23 mmol, 1.67 mol/l) of a solution of phenyl lithium in dibutyl ether was slowly added to the ice-cooled suspension and the mixture was allowed to warm to rt. After stirring for 4 h the reaction mixture was carefully quenched by adding 15 ml $H_2O$, extracted with $CH_2Cl_2$ and evaporated to dryness. The crude product was purified by column chromatography on silica gel (h = 20 cm, ø = 3 cm, 100 % cyclohexane) to afford 430 mg (81 %) of **1** as colourless crystals.

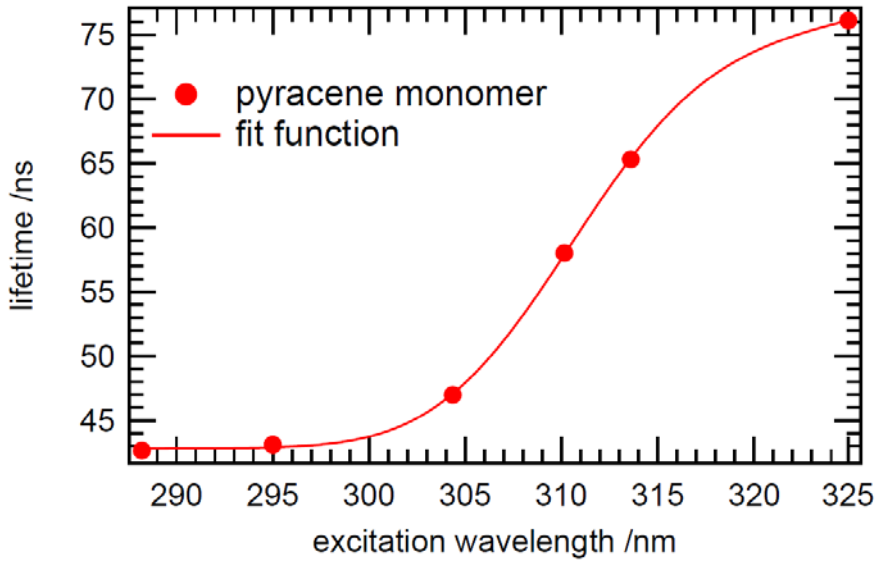
**Fp.** 205-219 °C
**$^1$H-NMR** (400 MHz, $CDCl_3$): δ = 7.19 (s, 4H, C$H_{arom.}$), 3.42 (s, 8H, C$H_2$) ppm.
**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ = 141.0 ($C_q$), 138.5 ($C_q$), 120.5 ($C_t$H), 31.8 ($C_s$$H_2$) ppm.
**FT-IR (ATR):** $\tilde{\nu}$= 2962 (w), 2917 (m), 2833 (m), 1571 (w), 1435 (w), 1418 (m), 1019 (m), 839 (s), 783 (s) $cm^{-1}$.
**MS** (EI, 70 eV): m/z (%) = 180.1 ([$M^+$], 100), 165.1 ([$M^+$ - $CH_3$], 47), 152.1 ([$M^+$ - $C_2H_4$], 16), 76.1 ([$C_6H_4{}^+$], 12).

## B) REMPI-Spectrum of Pyracene, Recorded with ps-Laser

The spectrum gives an impression of the quality of a wavelengths scan recorded with the ps-laser system.

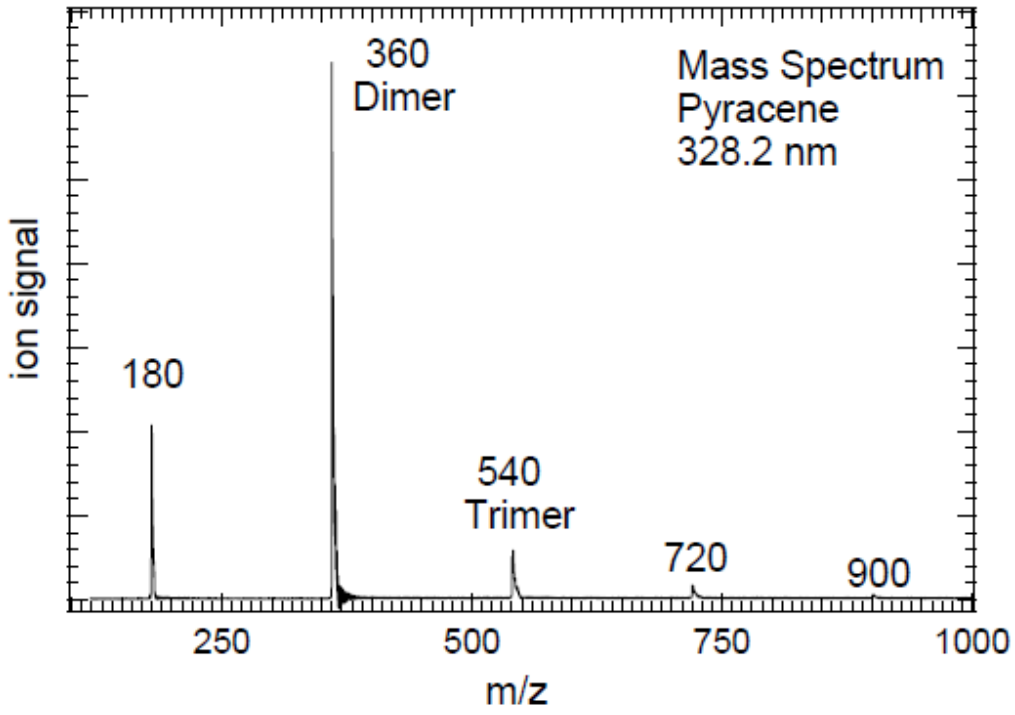



## C) Lifetimes of Pyracene as a function of excitation wavelengths.



## D) Mass Spectrum of Pyracene Clusters:

Mass Spectrum recorded with the ps-laser at 328.2 nm, close to the maximum of the first band of the dimer electronic spectrum.



## E) Computed Vibrational Wavenumbers of the $S_0$ state

Vibrational wavenumbers in the $S_0$ state of pyracene, computed by DFT and used to assign the IR- and Raman spectrum. SCS-MP2 yielded significantly different values only for $7a_u$ and $6b_{1g}$ (see table 3 of main paper)

| | v1 | v2 | v3 | v4 | v5 | v6 | v7 | v8 | v9 | v10 | v11 | v12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $12a_g$ | 3204 | 3080 | 1752 | 1515 | 1501 | 1411 | 1251 | 1155 | 1089 | 935 | 651 | 484 |
| $7a_u$ | 3103 | 1244 | 1031 | 941 | 634 | 310 | 96 | | | | | |
| $6b_{1g}$ | 3103 | 1245 | 1026 | 830 | 467 | 114 | | | | | | |
| $11b_{1u}$ | 3187 | 3079 | 1663 | 1504 | 1480 | 1298 | 1250 | 943 | 940 | 779 | 534 | |
| $11b_{1g}$ | 3187 | 3069 | 1706 | 1541 | 1477 | 1328 | 1242 | 1158 | 791 | 541 | 506 | |
| $7b_{1u}$ | 3122 | 1181 | 872 | 807 | 608 | 152 | 124 | | | | | |
| $7b_{1g}$ | 3122 | 1177 | 962 | 867 | 759 | 463 | 311 | | | | | |
| $11b_{1u}$ | 3203 | 3069 | 1565 | 1477 | 1392 | 1285 | 1267 | 1084 | 974 | 667 | 387 | |

## F) Computed Vibrational Wavenumbers of the $S_1$ state

Vibrational wavenumbers in the $S_1$ state of pyracene, computed by SCS-CC2.

| | $12a_g$ | $7a_u$ | $6b_{1g}$ | $11b_{1u}$ | $11b_{2g}$ | $7b_{2u}$ | $7b_{3g}$ | $11b_{3u}$ |
|---|---|---|---|---|---|---|---|---|
| v1 | 3210 | 3096 | 3096 | 3193 | 3191 | 3114 | 3114 | 3208 |
| v2 | 3065 | 1219 | 1220 | 3064 | 3052 | 1143 | 1142 | 3052,3 |
| v3 | 1677 | 984 | 992 | 1482 | 1631 | 796 | 785 | 1764 |
| v4 | 1533 | 719 | 663 | 1473 | 1461 | 657 | 730 | 1463 |
| v5 | 1481 | 405 | 386 | 1438 | 1448 | 465 | 354 | 1436 |
| v6 | 1341 | 227 | 58 | 1265 | 1309 | 147 | 288 | 1306 |
| v7 | 1214 | 41 | | 1209 | 1189 | 54 | 190 | 1176 |
| v8 | 1146 | | | 936 | 1104 | | | 1060 |
| v9 | 1040 | | | 911 | 747 | | | 929 |
| v10 | 930 | | | 754 | 513 | | | 635 |
| v11 | 625 | | | 499 | 424 | | | 357 |
| v12 | 453 | | | | | | | |

## G) List of Peaks Observed in the REMPI Spectrum

List of Peaks observed in the [1+1] REMPI experiments on pyracene. At energies above 1000 $cm^{-1}$ very weak bands were ignored due to the small number of scans. Note that at higer energies no unambiguous assignments are possible. Therefore fundamentals are labelled A, B, C..

| Peak Position /$cm^{-1}$ | Assignment | Intensity[1] |
|---|---|---|
| 30798 | $0^0$ | s |
| +71 | $7a_u^2$ | vw |
| +121 | $7b_{2u}^2$ | s |
| +194 | $7b_{2u}^2 7a_u^2$ | w |
| +206 | | vw |
| +233 | | vw |
| +256 | $7b_{2u}^4$ | w |
| +297 | $6b_{2u}^2$ | w |
| +375 (??) | | vw |
| +424 | $11b_{2g}$ | s |
| +453 | $5b_{2u}7b_{2u}$ | m |
| +482 | $12a_g$ | m |
| +516 | | w |
| +524 | | w |
| +546 | $11b_{2g}7b_{2u}^2$ | m |
| +604 | $12a_g7b_{2u}^2$ | m |
| +615 | $10b_{2g}$ | s |
| +654 | $11a_g$ | s |
| +680 | $11b_{2g}7b_{2u}^4$ | vw |
| +688 | $10b_{2g}7a_u^2$ | vw |
| +708 | | w |
| +739 | $10b_{2g}7b_{2u}^2$ | s |
| +750 | $9b_{2g}$ | m |
| +761 | $3b_{2u}^1 7b_{2u}^1$ | m |
| +770 | $11a_g7b_{2u}^2$ | m |
| +785 | | w |
| +809 | $10b_{2g}\ 7b_{2u}^2 7a_u^2$ | m |
| +824 | $10b_{2g}$ + 206 | w |
| +851 | $11b_{2g}^2$ | m |
| +857 | | vw |
| +870 | $10b_{2g}\ 7b_{2u}^4$ or $9b_{2g}7b_{2u}^2$ | w |
| +880 | | w |
| +888 | | w |
| +902 | $12a_g11b_{2g}$ | m |
| +909 | $10b_{2g}6b_{2u}^2$ or $11a_g7b_{2u}^4$ | w |
| +933 | | vw |

| | | |
|---|---|---|
| +984 | $11b_{2g}^{2}7b_{2u}^{2}$ | m |
| +1023 | $12a_g11b_{2g}7b_{2u}^{2}$ | w |
| +1029 | $10b_{2g}6b_{2u}^{2}7b_{2u}^{2}$ | m |
| +1043 | $10b_{2g}11b_{2g}$ | m |
| +1072 | $9a_g$ (or $11a_g6b_{2u}^{2}7b_{2u}^{2}$) | m |
| +1080 | $11b_{2g}11a_g$ | m |
| +1109 | $11b_{2g}^{2}7b_{2u}^{4}$ | m |
| +1114 | $A^1$ (8 $a_g$ and/or 7 $b_{2g}$) | s |
| +1120 | | w |
| +1164 | $10b_{2g}11b_{2g}7b_{2u}^{2}$ | w |
| +1172 | | w |
| +1177 | | w |
| +1194 | $9a_g7b_{2u}^{2}$ | s |
| +1210 | | w |
| +1215 | | w |
| +1233 | $10b_{2g}^{2}$ or $A^1 7b_{2u}^{2}$ | s |
| +1260 | $11a_g9b_{2g}$ | m |
| +1266 | | m |
| +1299 | | w |
| +1319 | | w |
| +1325 | $9a_g7b_{2u}^{4}$ | m |
| +1336 | | m |
| +1356 | $10b_{2g}^{2}\,7b_{2u}^{2}$ | m |
| +1368 | $A^1 7b_{2u}^{4}$ | w |
| +1380 | | w |
| +1391 | $11a_g10b_{2g}\,7b_{2u}^{2}$ | m |
| +1396 | $B^1$ ($6a_g$ or $5b_{2g}$) | m |
| +1427 | | w |
| +1439 | | w |
| +1444 | | w |
| +1457 | $C^1$ ($5a_g$ or $4b_{2g}$ or $5b_{2g}$) | s |
| +1464 | $B_1 7a_u^{2}$ | w |
| +1480 | | w |
| +1518 | $B^1 7b_{2u}^{2}$ | w |
| +1526 | $D^1$ ($4a_g$) | s |
| +1552 | | m |
| +1562 | | m |
| +1571 | $C^1 7b_{2u}^{2}$ | s |
| +1578 | | w |
| +1618 | | w |
| +1639 | $E^1$ ($3a_g$ or $3b_{2g}$) | s |
| +1647 | $D^1 7b_{2u}^{2}$ | m |
| | | |
| | | |

[1] s=strong, m=medium, w=weak, vw=very weak

# H) Stationary points of the ab initio computations

**Table H1: Optimised geometries.**

**Ground state $S_0$**

| | | | |
|---|---|---|---|
| C | 0.789699 | 0.000000 | 2.901922 |
| C | 1.187755 | 0.000000 | 1.430605 |
| C | 0.000000 | 0.000000 | 0.689860 |
| C | -1.187755 | 0.000000 | 1.430605 |
| C | -0.789699 | 0.000000 | 2.901922 |
| C | 0.000000 | 0.000000 | -0.689860 |
| C | 1.187755 | 0.000000 | -1.430605 |
| C | 2.376964 | 0.000000 | -0.718794 |
| C | 2.376964 | 0.000000 | 0.718794 |
| C | -1.187755 | 0.000000 | -1.430605 |
| C | -0.789699 | 0.000000 | -2.901922 |
| C | 0.789699 | 0.000000 | -2.901922 |
| C | -2.376964 | 0.000000 | 0.718794 |
| C | -2.376964 | 0.000000 | -0.718794 |
| H | 3.333408 | 0.000000 | -1.228208 |
| H | 3.333408 | 0.000000 | 1.228208 |
| H | -3.333408 | 0.000000 | -1.228208 |
| H | -3.333408 | 0.000000 | 1.228208 |
| H | 1.178285 | 0.877615 | 3.420425 |
| H | -1.178285 | -0.877615 | 3.420425 |
| H | 1.178285 | -0.877615 | 3.420425 |
| H | -1.178285 | 0.877615 | 3.420425 |
| H | -1.178285 | -0.877615 | -3.420425 |
| H | -1.178285 | 0.877615 | -3.420425 |
| H | 1.178285 | -0.877615 | -3.420425 |
| H | 1.178285 | 0.877615 | -3.420425 |

**$S_1$ $D_2h$**

| | | | |
|---|---|---|---|
| C | 0.794823 | 0.000000 | 2.936637 |
| C | 1.192596 | 0.000000 | 1.459000 |
| C | 0.000000 | 0.000000 | 0.719077 |
| C | -1.192596 | 0.000000 | 1.459000 |
| C | -0.794823 | 0.000000 | 2.936637 |
| C | 0.000000 | 0.000000 | -0.719077 |
| C | 1.192596 | 0.000000 | -1.459000 |
| C | 2.429576 | 0.000000 | -0.731661 |
| C | 2.429576 | 0.000000 | 0.731661 |
| C | -1.192596 | 0.000000 | -1.459000 |
| C | -0.794823 | 0.000000 | -2.936637 |
| C | 0.794823 | 0.000000 | -2.936637 |
| C | -2.429576 | 0.000000 | 0.731661 |
| C | -2.429576 | 0.000000 | -0.731661 |

| | | | |
|---|---|---|---|
| H | 3.392827 | 0.000000 | -1.254043 |
| H | 3.392827 | 0.000000 | 1.254043 |
| H | -3.392827 | 0.000000 | -1.254043 |
| H | -3.392827 | 0.000000 | 1.254043 |
| H | 1.193113 | 0.888265 | 3.459476 |
| H | -1.193113 | -0.888265 | 3.459476 |
| H | 1.193113 | -0.888265 | 3.459476 |
| H | -1.193113 | 0.888265 | 3.459476 |
| H | -1.193113 | -0.888265 | -3.459476 |
| H | -1.193113 | 0.888265 | -3.459476 |
| H | 1.193113 | -0.888265 | -3.459476 |
| H | 1.193113 | 0.888265 | -3.459476 |

**$S_2$ $D_2h$**

| | | | |
|---|---|---|---|
| C | 0.795954 | 0.000000 | 2.917455 |
| C | 1.192317 | 0.000000 | 1.443187 |
| C | 0.000000 | 0.000000 | 0.703190 |
| C | -1.192317 | 0.000000 | 1.443187 |
| C | -0.795954 | 0.000000 | 2.917455 |
| C | 0.000000 | 0.000000 | -0.703190 |
| C | 1.192317 | 0.000000 | -1.443187 |
| C | 2.448073 | 0.000000 | -0.705107 |
| C | 2.448073 | 0.000000 | 0.705107 |
| C | -1.192317 | 0.000000 | -1.443187 |
| C | -0.795954 | 0.000000 | -2.917455 |
| C | 0.795954 | 0.000000 | -2.917455 |
| C | -2.448073 | 0.000000 | 0.705107 |
| C | -2.448073 | 0.000000 | -0.705107 |
| H | 3.406359 | 0.000000 | -1.237227 |
| H | 3.406359 | 0.000000 | 1.237227 |
| H | -3.406359 | 0.000000 | -1.237227 |
| H | -3.406359 | 0.000000 | 1.237227 |
| H | 1.192861 | 0.887389 | 3.446369 |
| H | -1.192861 | -0.887389 | 3.446369 |
| H | 1.192861 | -0.887389 | 3.446369 |
| H | -1.192861 | 0.887389 | 3.446369 |
| H | -1.192861 | -0.887389 | -3.446369 |
| H | -1.192861 | 0.887389 | -3.446369 |
| H | 1.192861 | -0.887389 | -3.446369 |
| H | 1.192861 | 0.887389 | -3.446369 |

**$S_2$ $D_2$**

| | | | |
|---|---|---|---|
| C | 2.447627 | 0.000732 | 0.705180 |
| C | 1.192281 | -0.004337 | 1.443793 |
| C | 0.000000 | 0.000000 | 0.703054 |
| C | -1.192281 | 0.004337 | 1.443793 |
| C | -2.447627 | -0.000732 | 0.705180 |
| C | -2.447627 | 0.000732 | -0.705180 |
| C | -1.192281 | -0.004337 | -1.443793 |
| C | 0.000000 | 0.000000 | -0.703054 |
| C | 1.192281 | 0.004337 | -1.443793 |
| C | 2.447627 | -0.000732 | -0.705180 |
| H | 3.406054 | 0.000402 | -1.237016 |
| H | 3.406054 | -0.000402 | 1.237016 |
| H | -3.406054 | 0.000402 | 1.237016 |
| H | -3.406054 | -0.000402 | -1.237016 |

| | | | |
|---|---|---|---|
| C | 0.791841 | -0.073018 | -2.914877 |
| C | -0.791841 | 0.073018 | -2.914877 |
| C | 0.791841 | 0.073018 | 2.914877 |
| C | -0.791841 | -0.073018 | 2.914877 |
| H | -1.085877 | -1.051935 | 3.344449 |
| H | 1.085877 | 1.051935 | 3.344449 |
| H | 1.085877 | -1.051935 | -3.344449 |
| H | -1.085877 | 1.051935 | -3.344449 |
| H | 1.274451 | 0.704855 | -3.533545 |
| H | -1.274451 | -0.704855 | -3.533545 |
| H | -1.274451 | 0.704855 | 3.533545 |
| H | 1.274451 | -0.704855 | 3.533545 |

**$S_2$ $C_{2h}$**

| | | | |
|---|---|---|---|
| C | -2.444278 | 0.024842 | 0.705413 |
| C | -1.191065 | 0.047205 | 1.444473 |
| C | 0.000000 | 0.000000 | 0.702474 |
| C | 1.191065 | -0.047205 | 1.444473 |
| C | 2.444278 | -0.024842 | 0.705413 |
| C | 2.444278 | -0.024842 | -0.705413 |
| C | 1.191065 | -0.047205 | -1.444473 |
| C | 0.000000 | 0.000000 | -0.702474 |
| C | -1.191065 | 0.047205 | -1.444473 |
| C | -2.444278 | 0.024842 | -0.705413 |
| H | -3.402909 | 0.015205 | -1.236727 |
| H | -3.402909 | 0.015205 | 1.236727 |
| H | 3.402909 | -0.015205 | 1.236727 |
| H | 3.402909 | -0.015205 | -1.236727 |
| C | -0.789322 | -0.082403 | -2.910826 |
| C | 0.789322 | 0.082403 | -2.910826 |
| C | -0.789322 | -0.082403 | 2.910826 |
| C | 0.789322 | 0.082403 | 2.910826 |
| H | 1.060541 | 1.093342 | 3.281255 |
| H | -1.060541 | -1.093342 | 3.281255 |
| H | -1.284119 | 0.648936 | -3.572901 |
| H | 1.284119 | -0.648936 | -3.572901 |
| H | -1.060541 | -1.093342 | -3.281255 |
| H | 1.060541 | 1.093342 | -3.281255 |
| H | 1.284119 | -0.648936 | 3.572901 |
| H | -1.284119 | 0.648936 | 3.572901 |

**Table H2: Start geometries for optimization of $S_2$ twisted structure.**

**$C_{2h}$ (+ +/ - -)**

| | | | |
|---|---|---|---|
| C | 0.718400 | -0.024700 | -2.377000 |
| C | 1.429800 | -0.049300 | -1.187800 |
| C | 0.689400 | -0.023700 | 0.000000 |
| C | 1.429800 | -0.049300 | 1.187800 |
| C | 0.718400 | -0.024700 | 2.377000 |
| C | -0.718400 | 0.024700 | 2.377000 |

| | | | |
|---|---|---|---|
| C | -1.429800 | 0.049300 | 1.187800 |
| C | -0.689400 | 0.023700 | 0.000000 |
| C | -1.429800 | 0.049300 | -1.187800 |
| C | -0.718400 | 0.024700 | -2.377000 |
| H | -1.227500 | 0.042300 | -3.333400 |
| H | 1.227500 | -0.042300 | -3.333400 |
| H | 1.227500 | -0.042300 | 3.333400 |
| H | -1.227500 | 0.042300 | 3.333400 |
| C | -2.870800 | -0.026900 | -0.778500 |
| C | -2.870800 | -0.026900 | 0.778500 |
| C | 2.870800 | 0.026900 | -0.778500 |
| C | 2.870800 | 0.026900 | 0.778500 |
| H | 3.432000 | -0.836500 | 1.133000 |
| H | 3.337900 | 0.944500 | -1.133000 |
| H | -3.337900 | -0.944500 | -1.133000 |
| H | -3.432000 | 0.836500 | 1.133000 |
| H | -3.432000 | 0.836500 | -1.133000 |
| H | -3.337900 | -0.944500 | 1.133000 |
| H | 3.337900 | 0.944500 | 1.133000 |
| H | 3.432000 | -0.836500 | -1.133000 |

**$C_{2v}$ (+ +/ + +)**

| | | | |
|---|---|---|---|
| C | -0.718800 | -2.377000 | 0.071769 |
| C | -1.430600 | -1.187800 | 0.071769 |
| C | -0.689900 | 0.000000 | 0.071769 |
| C | -1.430600 | 1.187800 | 0.071769 |
| C | -0.718800 | 2.377000 | 0.071769 |
| C | 0.718800 | 2.377000 | 0.071769 |
| C | 1.430600 | 1.187800 | 0.071769 |
| C | 0.689900 | 0.000000 | 0.071769 |
| C | 1.430600 | -1.187800 | 0.071769 |
| C | 0.718800 | -2.377000 | 0.071769 |
| H | 1.228200 | -3.333400 | 0.071769 |
| H | -1.228200 | -3.333400 | 0.071769 |
| H | -1.228200 | 3.333400 | 0.071769 |
| H | 1.228200 | 3.333400 | 0.071769 |
| C | 2.868200 | -0.778500 | -0.053831 |
| C | 2.868200 | 0.778500 | -0.053831 |
| C | -2.868200 | -0.778500 | -0.053831 |
| C | -2.868200 | 0.778500 | -0.053831 |
| H | -3.303400 | 1.133000 | -0.987031 |
| H | -3.458700 | -1.133000 | 0.789669 |
| H | 3.303400 | -1.133000 | -0.987031 |
| H | 3.458700 | 1.133000 | 0.789669 |
| H | 3.458700 | -1.133000 | 0.789669 |
| H | 3.303400 | 1.133000 | -0.987031 |
| H | -3.458700 | 1.133000 | 0.789669 |
| H | -3.303400 | -1.133000 | -0.987031 |

**Table H3: Optimized structures of pyracene dimers**

**Crossed**

| | | | |
|---|---|---|---|
| C | 2.614646 | -1.494573 | -1.753033 |
| C | 1.856990 | -0.171575 | -1.758722 |
| C | 0.489258 | -0.489258 | -1.745798 |
| C | 0.171575 | -1.856990 | -1.758722 |
| C | 1.494573 | -2.614646 | -1.753033 |
| C | -0.489258 | 0.489258 | -1.745798 |
| C | -0.171575 | 1.856990 | -1.758722 |
| C | 1.174816 | 2.194518 | -1.782447 |
| C | 2.194518 | 1.174816 | -1.782447 |
| C | -1.856990 | 0.171575 | -1.758722 |
| C | -2.614646 | 1.494573 | -1.753033 |
| C | -1.494573 | 2.614646 | -1.753033 |
| C | -1.174816 | -2.194518 | -1.782447 |
| C | -2.194518 | -1.174816 | -1.782447 |
| H | 1.491607 | 3.241214 | -1.806042 |
| H | 3.241214 | 1.491607 | -1.806042 |
| H | -3.241214 | -1.491607 | -1.806042 |
| H | -1.491607 | -3.241214 | -1.806042 |
| H | 3.251705 | -1.579787 | -0.858233 |
| H | 1.590049 | -3.275970 | -2.630095 |
| H | 3.275970 | -1.590049 | -2.630095 |
| H | 1.579787 | -3.251705 | -0.858233 |
| H | -3.275970 | 1.590049 | -2.630095 |
| H | -3.251705 | 1.579787 | -0.858233 |
| H | -1.590049 | 3.275970 | -2.630095 |
| H | -1.579787 | 3.251705 | -0.858233 |
| C | 1.494573 | 2.614646 | 1.753033 |
| C | 0.171575 | 1.856990 | 1.758722 |
| C | 0.489258 | 0.489258 | 1.745798 |
| C | 1.856990 | 0.171575 | 1.758722 |
| C | 2.614646 | 1.494573 | 1.753033 |
| C | -0.489258 | -0.489258 | 1.745798 |
| C | -1.856990 | -0.171575 | 1.758722 |
| C | -2.194518 | 1.174816 | 1.782447 |
| C | -1.174816 | 2.194518 | 1.782447 |
| C | -0.171575 | -1.856990 | 1.758722 |
| C | -1.494573 | -2.614646 | 1.753033 |
| C | -2.614646 | -1.494573 | 1.753033 |
| C | 2.194518 | -1.174816 | 1.782447 |
| C | 1.174816 | -2.194518 | 1.782447 |
| H | -3.241214 | 1.491607 | 1.806042 |
| H | -1.491607 | 3.241214 | 1.806042 |
| H | 1.491607 | -3.241214 | 1.806042 |
| H | 3.241214 | -1.491607 | 1.806042 |
| H | 1.590049 | 3.275970 | 2.630095 |
| H | 3.251705 | 1.579787 | 0.858233 |
| H | 1.579787 | 3.251705 | 0.858233 |
| H | 3.275970 | 1.590049 | 2.630095 |
| H | -1.579787 | -3.251705 | 0.858233 |
| H | -1.590049 | -3.275970 | 2.630095 |
| H | -3.251705 | -1.579787 | 0.858233 |
| H | -3.275970 | -1.590049 | 2.630095 |

**Shift z**

| | | | |
|---|---|---|---|
| C | -1.397050 | 1.648527 | 0.791707 |
| C | -1.735770 | 0.217157 | 1.191587 |
| C | -1.914863 | -0.504933 | 0.000000 |
| C | -1.735770 | 0.217157 | -1.191587 |
| C | -1.397050 | 1.648527 | -0.791707 |
| C | -2.206040 | -1.859052 | 0.000000 |
| C | -2.340477 | -2.589114 | 1.192835 |
| C | -2.169243 | -1.894468 | 2.383626 |
| C | -1.864224 | -0.484947 | 2.382505 |
| C | -2.340477 | -2.589114 | -1.192835 |
| C | -2.630273 | -4.033157 | -0.792653 |
| C | -2.630273 | -4.033157 | 0.792653 |
| C | -1.864224 | -0.484947 | -2.382505 |
| C | -2.169243 | -1.894468 | -2.383626 |
| H | -2.252459 | -2.403706 | 3.348081 |
| H | -1.722534 | 0.013957 | 3.345034 |
| H | -2.252459 | -2.403706 | -3.348081 |
| H | -1.722534 | 0.013957 | -3.345034 |
| H | -0.413753 | 1.945949 | 1.187043 |
| H | -2.134542 | 2.364202 | -1.191571 |
| H | -2.134542 | 2.364202 | 1.191571 |
| H | -0.413753 | 1.945949 | -1.187043 |
| H | -3.600068 | -4.376917 | -1.189081 |
| H | -1.867475 | -4.723551 | -1.189490 |
| H | -3.600068 | -4.376917 | 1.189081 |
| H | -1.867475 | -4.723551 | 1.189490 |
| C | 2.630273 | 4.033157 | 0.792653 |
| C | 2.340477 | 2.589114 | 1.192835 |
| C | 2.206040 | 1.859052 | 0.000000 |
| C | 2.340477 | 2.589114 | -1.192835 |
| C | 2.630273 | 4.033157 | -0.792653 |
| C | 1.914863 | 0.504933 | 0.000000 |
| C | 1.735770 | -0.217157 | 1.191587 |
| C | 1.864224 | 0.484947 | 2.382505 |
| C | 2.169243 | 1.894468 | 2.383626 |
| C | 1.735770 | -0.217157 | -1.191587 |
| C | 1.397050 | -1.648527 | -0.791707 |
| C | 1.397050 | -1.648527 | 0.791707 |
| C | 2.169243 | 1.894468 | -2.383626 |
| C | 1.864224 | 0.484947 | -2.382505 |
| H | 1.722534 | -0.013957 | 3.345034 |
| H | 2.252459 | 2.403706 | 3.348081 |
| H | 1.722534 | -0.013957 | -3.345034 |
| H | 2.252459 | 2.403706 | -3.348081 |
| H | 3.600068 | 4.376917 | 1.189081 |
| H | 1.867475 | 4.723551 | -1.189490 |
| H | 1.867475 | 4.723551 | 1.189490 |
| H | 3.600068 | 4.376917 | -1.189081 |
| H | 0.413753 | -1.945949 | -1.187043 |
| H | 2.134542 | -2.364202 | -1.191571 |
| H | 0.413753 | -1.945949 | 1.187043 |
| H | 2.134542 | -2.364202 | 1.191571 |

**Shift x**

| | | | |
|---|---|---|---|
| C | 0.192983 | -1.824760 | 2.903833 |
| C | 0.588589 | -1.730143 | 1.432933 |
| C | -0.599355 | -1.831948 | 0.691879 |
| C | -1.787795 | -1.932075 | 1.432782 |
| C | -1.390265 | -1.879114 | 2.904590 |
| C | -0.599355 | -1.831948 | -0.691879 |
| C | 0.588589 | -1.730143 | -1.432933 |
| C | 1.772497 | -1.598372 | -0.720459 |
| C | 1.772497 | -1.598372 | 0.720459 |
| C | -1.787795 | -1.932075 | -1.432782 |
| C | -1.390265 | -1.879114 | -2.904590 |
| C | 0.192983 | -1.824760 | -2.903833 |
| C | -2.975300 | -2.028844 | 0.721031 |
| C | -2.975300 | -2.028844 | -0.721031 |
| H | 2.730824 | -1.489001 | -1.234630 |
| H | 2.730824 | -1.489001 | 1.234630 |
| H | -3.936387 | -2.105981 | -1.237538 |
| H | -3.936387 | -2.105981 | 1.237538 |
| H | 0.569706 | -0.977199 | 3.496659 |
| H | -1.761726 | -2.750062 | 3.468518 |
| H | 0.612907 | -2.736047 | 3.362202 |
| H | -1.815300 | -0.985539 | 3.392438 |
| H | -1.761726 | -2.750062 | -3.468518 |
| H | -1.815300 | -0.985539 | -3.392438 |
| H | 0.612907 | -2.736047 | -3.362202 |
| H | 0.569706 | -0.977199 | -3.496659 |
| C | 1.390265 | 1.879114 | 2.904590 |
| C | 1.787795 | 1.932075 | 1.432782 |
| C | 0.599355 | 1.831948 | 0.691879 |
| C | -0.588589 | 1.730143 | 1.432933 |
| C | -0.192983 | 1.824760 | 2.903833 |
| C | 0.599355 | 1.831948 | -0.691879 |
| C | 1.787795 | 1.932075 | -1.432782 |
| C | 2.975300 | 2.028844 | -0.721031 |
| C | 2.975300 | 2.028844 | 0.721031 |
| C | -0.588589 | 1.730143 | -1.432933 |
| C | -0.192983 | 1.824760 | -2.903833 |
| C | 1.390265 | 1.879114 | -2.904590 |
| C | -1.772497 | 1.598372 | 0.720459 |
| C | -1.772497 | 1.598372 | -0.720459 |
| H | 3.936387 | 2.105981 | -1.237538 |
| H | 3.936387 | 2.105981 | 1.237538 |
| H | -2.730824 | 1.489001 | -1.234630 |
| H | -2.730824 | 1.489001 | 1.234630 |
| H | 1.761726 | 2.750062 | 3.468518 |
| H | -0.569706 | 0.977199 | 3.496659 |
| H | 1.815300 | 0.985539 | 3.392438 |
| H | -0.612907 | 2.736047 | 3.362202 |
| H | -0.569706 | 0.977199 | -3.496659 |
| H | -0.612907 | 2.736047 | -3.362202 |
| H | 1.815300 | 0.985539 | -3.392438 |
| H | 1.761726 | 2.750062 | -3.468518 |

**Cofacial**

| | | | |
|---|---|---|---|
| C | 2.905178 | 0.792430 | -1.971088 |
| C | 1.433143 | 1.192538 | -1.941306 |
| C | 0.692163 | 0.000000 | -1.929965 |
| C | 1.433143 | -1.192538 | -1.941306 |
| C | 2.905178 | -0.792430 | -1.971088 |
| C | -0.692163 | 0.000000 | -1.929965 |
| C | -1.433143 | 1.192538 | -1.941306 |
| C | -0.720564 | 2.383439 | -1.938540 |
| C | 0.720564 | 2.383439 | -1.938540 |
| C | -1.433143 | -1.192538 | -1.941306 |
| C | -2.905178 | -0.792430 | -1.971088 |
| C | -2.905178 | 0.792430 | -1.971088 |
| C | 0.720564 | -2.383439 | -1.938540 |
| C | -0.720564 | -2.383439 | -1.938540 |
| H | -1.236527 | 3.347669 | -1.938516 |
| H | 1.236527 | 3.347669 | -1.938516 |
| H | -1.236527 | -3.347669 | -1.938516 |
| H | 1.236527 | -3.347669 | -1.938516 |
| H | 3.452946 | 1.190471 | -1.101744 |
| H | 3.412348 | -1.187991 | -2.866764 |
| H | 3.412348 | 1.187991 | -2.866764 |
| H | 3.452946 | -1.190471 | -1.101744 |
| H | -3.412348 | -1.187991 | -2.866764 |
| H | -3.452946 | -1.190471 | -1.101744 |
| H | -3.412348 | 1.187991 | -2.866764 |
| H | -3.452946 | 1.190471 | -1.101744 |
| C | 2.905178 | 0.792430 | 1.971088 |
| C | 1.433143 | 1.192538 | 1.941306 |
| C | 0.692163 | 0.000000 | 1.929965 |
| C | 1.433143 | -1.192538 | 1.941306 |
| C | 2.905178 | -0.792430 | 1.971088 |
| C | -0.692163 | 0.000000 | 1.929965 |
| C | -1.433143 | 1.192538 | 1.941306 |
| C | -0.720564 | 2.383439 | 1.938540 |
| C | 0.720564 | 2.383439 | 1.938540 |
| C | -1.433143 | -1.192538 | 1.941306 |
| C | -2.905178 | -0.792430 | 1.971088 |
| C | -2.905178 | 0.792430 | 1.971088 |
| C | 0.720564 | -2.383439 | 1.938540 |
| C | -0.720564 | -2.383439 | 1.938540 |
| H | -1.236527 | 3.347669 | 1.938516 |
| H | 1.236527 | 3.347669 | 1.938516 |
| H | -1.236527 | -3.347669 | 1.938516 |
| H | 1.236527 | -3.347669 | 1.938516 |
| H | 3.412348 | 1.187991 | 2.866764 |
| H | 3.452946 | -1.190471 | 1.101744 |
| H | 3.452946 | 1.190471 | 1.101744 |
| H | 3.412348 | -1.187991 | 2.866764 |
| H | -3.452946 | -1.190471 | 1.101744 |
| H | -3.412348 | -1.187991 | 2.866764 |
| H | -3.452946 | 1.190471 | 1.101744 |
| H | -3.412348 | 1.187991 | 2.866764 |

**T-shaped I**

| | | | |
|---|---|---|---|
| C | 2.906494 | 0.792466 | -3.126201 |
| C | 1.434193 | 1.192653 | -3.150937 |
| C | 0.692238 | 0.000000 | -3.168193 |
| C | 1.434193 | -1.192653 | -3.150937 |
| C | 2.906494 | -0.792466 | -3.126201 |
| C | -0.692238 | 0.000000 | -3.168193 |
| C | -1.434193 | 1.192653 | -3.150937 |
| C | -0.720863 | 2.383917 | -3.138628 |
| C | 0.720863 | 2.383917 | -3.138628 |
| C | -1.434193 | -1.192653 | -3.150937 |
| C | -2.906494 | -0.792466 | -3.126201 |
| C | -2.906494 | 0.792466 | -3.126201 |
| C | 0.720863 | -2.383917 | -3.138628 |
| C | -0.720863 | -2.383917 | -3.138628 |
| H | -1.236742 | 3.347995 | -3.119651 |
| H | 1.236742 | 3.347995 | -3.119651 |
| H | -1.236742 | -3.347995 | -3.119651 |
| H | 1.236742 | -3.347995 | -3.119651 |
| H | 3.416268 | 1.188705 | -2.232336 |
| H | 3.449987 | -1.190234 | -3.999083 |
| H | 3.449987 | 1.190234 | -3.999083 |
| H | 3.416268 | -1.188705 | -2.232336 |
| H | -3.449987 | -1.190234 | -3.999083 |
| H | -3.416268 | -1.188705 | -2.232336 |
| H | -3.449987 | 1.190234 | -3.999083 |
| H | -3.416268 | 1.188705 | -2.232336 |
| C | 0.000000 | 0.791334 | 0.225590 |
| C | 0.000000 | 1.192185 | 1.696139 |
| C | 0.000000 | 0.000000 | 2.439940 |
| C | 0.000000 | -1.192185 | 1.696139 |
| C | 0.000000 | -0.791334 | 0.225590 |
| C | 0.000000 | 0.000000 | 3.824728 |
| C | 0.000000 | 1.192842 | 4.566530 |
| C | 0.000000 | 2.383683 | 3.852541 |
| C | 0.000000 | 2.383300 | 2.410412 |
| C | 0.000000 | -1.192842 | 4.566530 |
| C | 0.000000 | -0.792678 | 6.039475 |
| C | 0.000000 | 0.792678 | 6.039475 |
| C | 0.000000 | -2.383300 | 2.410412 |
| C | 0.000000 | -2.383683 | 3.852541 |
| H | 0.000000 | 3.348331 | 4.368411 |
| H | 0.000000 | 3.347566 | 1.893973 |
| H | 0.000000 | -3.348331 | 4.368411 |
| H | 0.000000 | -3.347566 | 1.893973 |
| H | 0.877296 | 1.188466 | -0.308886 |
| H | -0.877296 | -1.188466 | -0.308886 |
| H | -0.877296 | 1.188466 | -0.308886 |
| H | 0.877296 | -1.188466 | -0.308886 |
| H | -0.883464 | -1.189237 | 6.567117 |
| H | 0.883464 | -1.189237 | 6.567117 |
| H | -0.883464 | 1.189237 | 6.567117 |
| H | 0.883464 | 1.189237 | 6.567117 |

**T-shaped II**

| | | | |
|---|---|---|---|
| C | 2.906006 | 0.792326 | -2.894327 |
| C | 1.434491 | 1.192387 | -2.936021 |
| C | 0.692402 | 0.000000 | -2.965747 |
| C | 1.434491 | -1.192387 | -2.936021 |
| C | 2.906006 | -0.792326 | -2.894327 |
| C | -0.692402 | 0.000000 | -2.965747 |
| C | -1.434491 | 1.192387 | -2.936021 |
| C | -0.721099 | 2.383735 | -2.917847 |
| C | 0.721099 | 2.383735 | -2.917847 |
| C | -1.434491 | -1.192387 | -2.936021 |
| C | -2.906006 | -0.792326 | -2.894327 |
| C | -2.906006 | 0.792326 | -2.894327 |
| C | 0.721099 | -2.383735 | -2.917847 |
| C | -0.721099 | -2.383735 | -2.917847 |
| H | -1.237012 | 3.347493 | -2.887372 |
| H | 1.237012 | 3.347493 | -2.887372 |
| H | -1.237012 | -3.347493 | -2.887372 |
| H | 1.237012 | -3.347493 | -2.887372 |
| H | 3.401610 | 1.187569 | -1.992475 |
| H | 3.460692 | -1.190727 | -3.759925 |
| H | 3.460692 | 1.190727 | -3.759925 |
| H | 3.401610 | -1.187569 | -1.992475 |
| H | -3.460692 | -1.190727 | -3.759925 |
| H | -3.401610 | -1.187569 | -1.992475 |
| H | -3.460692 | 1.190727 | -3.759925 |
| H | -3.401610 | 1.187569 | -1.992475 |
| C | 0.000000 | 2.907213 | 3.695219 |
| C | 0.000000 | 1.434378 | 4.097232 |
| C | 0.000000 | 0.692443 | 2.904546 |
| C | 0.000000 | 1.432400 | 1.711079 |
| C | 0.000000 | 2.905546 | 2.109665 |
| C | 0.000000 | -0.692443 | 2.904546 |
| C | 0.000000 | -1.434378 | 4.097232 |
| C | 0.000000 | -0.721256 | 5.288581 |
| C | 0.000000 | 0.721256 | 5.288581 |
| C | 0.000000 | -1.432400 | 1.711079 |
| C | 0.000000 | -2.905546 | 2.109665 |
| C | 0.000000 | -2.907213 | 3.695219 |
| C | 0.000000 | 0.720929 | 0.518654 |
| C | 0.000000 | -0.720929 | 0.518654 |
| H | 0.000000 | -1.236957 | 6.253238 |
| H | 0.000000 | 1.236957 | 6.253238 |
| H | 0.000000 | -1.235065 | -0.443848 |
| H | 0.000000 | 1.235065 | -0.443848 |
| H | 0.883403 | 3.434928 | 4.091887 |
| H | -0.883135 | 3.432725 | 1.711769 |
| H | -0.883403 | 3.434928 | 4.091887 |
| H | 0.883135 | 3.432725 | 1.711769 |
| H | -0.883135 | -3.432725 | 1.711769 |
| H | 0.883135 | -3.432725 | 1.711769 |
| H | -0.883403 | -3.434928 | 4.091887 |
| H | 0.883403 | -3.434928 | 4.091887 |

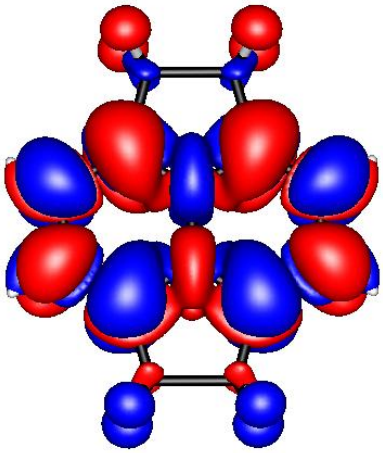
# I) Details of the Electronic Transitions

The leading configurations, the orbitals and the transition densities of the first two excited states are given on the SCS-CC2/cc-pVDZ level of theory. With this smaller basis set the most relevant features are more easily recognised, but the same qualitative picture is obtained in calculations with the large aug-cc-pVTZ basis.

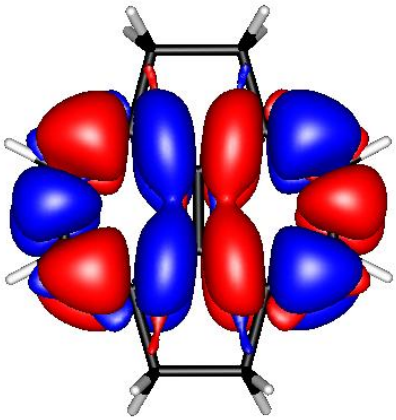
**Table I-1:** Leading configurations of the electronic transitions.

| **$S_1$ $b_3u$** | | | **$S_2$ $b_1u$** | | |
|---|---|---|---|---|---|
| Excitation energy /eV | Excitation | % | Excitation energy /eV | Excitation | % |
| 4.49 | HOMO→LUMO+1 | 58 | 4.82 | HOMO→LUMO | 93 |
| | HOMO-1→LUMO | 39 | | | |

**Figure I-1:** Transition densities of the electronic transitions.



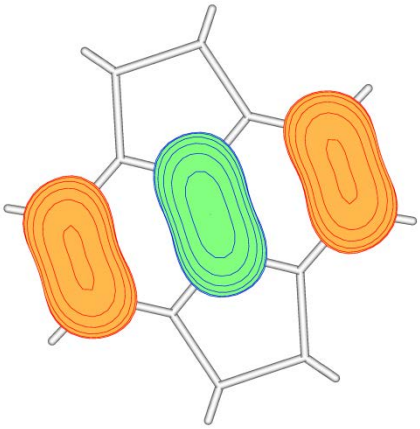
**Transition density $S_0 \rightarrow S_1$**



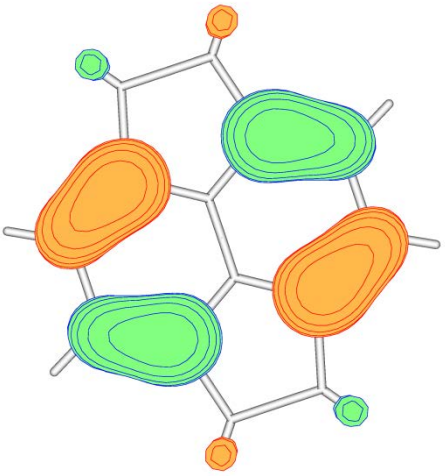
**Transition density $S_0 \rightarrow S_2$**

**Figure I-2:** Graphical representation of the four most important orbitals of pyracene.

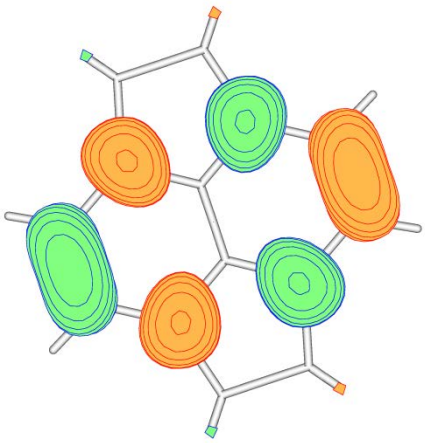
**HOMO-1**



**HOMO**



**LUMO**



**LUMO+1**