# Supplementary Materials: A Test of Various Partial Atomic Charge Models for Computations on Diheteroaryl Ketones and Thioketones

**Piotr Matczak**

Supplementary Material contains three sections: (S1) additional tables with the results of dipole moment calculations; (S2) selection of a quantum chemical method for calculating the reference full-density dipole moments of **1a–5a** and **1b–5b** from Figure 1; (S3) additional tables with the results of $E_{elst}$ calculations.

## S1. Additional Tables with the Results of Dipole Moment Calculations

**Table S1.** Dipole moments (μ in Debyes) calculated using the HF/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1a–5a** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Full Density** | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1a** | 5.24 | 5.75 | 8.54 | 6.28 | 19.63 | 3.74 | 5.29 | 5.26 | 4.78 | 5.22 | 5.24 |
| *ct*-**1a** | 4.26 | 3.81 | 6.07 | 4.57 | 11.73 | 3.27 | 4.13 | 4.28 | 4.10 | 4.29 | 4.27 |
| *tt*-**1a** | 2.99 | 1.55 | 2.78 | 2.38 | 0.79 | 2.68 | 2.65 | 3.04 | 3.00 | 3.03 | 3.01 |
| *cc*-**2a** | 4.75 | 3.81 | 2.11 | 2.10 | 6.68 | 2.60 | 3.93 | 4.75 | 4.37 | 4.65 | 4.74 |
| *ct*-**2a** | 3.75 | 3.43 | 4.92 | 4.91 | 7.78 | 2.86 | 3.65 | 3.79 | 3.58 | 3.75 | 3.76 |
| *tt*-**2a** | 2.63 | 3.06 | 7.33 | 9.19 | 8.91 | 3.17 | 3.39 | 2.64 | 2.55 | 2.71 | 2.65 |
| *cc*-**3a** | 4.61 | 3.92 | 0.93 | 4.98 | 3.33 | 2.95 | 4.28 | 4.69 | 3.97 | 4.41 | 4.61 |
| *ct*-**3a** | 3.64 | 3.35 | 5.09 | 6.27 | 7.94 | 2.77 | 3.38 | 3.67 | 3.27 | 3.63 | 3.64 |
| *tt*-**3a** | 2.56 | 2.75 | 8.33 | 11.80 | 11.78 | 2.63 | 2.45 | 3.67 | 2.70 | 2.70 | 2.55 |
| *cc*-**4a** | 0.60 | 1.70 | 2.56 | 1.92 | 12.75 | 0.67 | 1.23 | 0.68 | 0.54 | 0.65 | 0.62 |
| *ct*-**4a** | 3.51 | 3.00 | 4.80 | 3.88 | 9.29 | 2.85 | 3.37 | 3.56 | 3.45 | 3.53 | 3.53 |
| *tt*-**4a** | 5.53 | 3.85 | 6.55 | 5.40 | 5.63 | 4.48 | 4.99 | 5.57 | 5.41 | 5.56 | 5.57 |
| *cc*-**5a** | 0.12 | 0.34 | 1.71 | 0.11 | 9.29 | 0.15 | 0.41 | 0.19 | 0.05 | 0.20 | 0.15 |
| *ct*-**5a** | 3.70 | 3.47 | 4.93 | 4.54 | 8.12 | 3.08 | 3.53 | 3.69 | 3.60 | 3.66 | 3.70 |
| *tt*-**5a** | 5.48 | 5.19 | 6.97 | 6.64 | 7.64 | 4.66 | 5.27 | 5.50 | 5.48 | 5.48 | 5.50 |

**Table S2.** Dipole moments (μ in Debyes) calculated using the HF/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1b–5b** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Full Density** | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1b** | 5.21 | 5.38 | 5.82 | 1.70 | 9.55 | 3.68 | 4.86 | 5.30 | 4.69 | 5.26 | 5.25 |
| *ct*-**1b** | 4.58 | 3.96 | 3.92 | 1.31 | 5.58 | 3.44 | 3.98 | 4.67 | 4.64 | 4.75 | 4.63 |
| *tt*-**1b** | 3.63 | 2.41 | 0.79 | 1.17 | 7.44 | 3.08 | 2.79 | 3.77 | 3.83 | 3.83 | 3.71 |
| *cc*-**2b** | 4.92 | 3.76 | 0.21 | 6.02 | 2.80 | 2.72 | 3.73 | 5.05 | 4.34 | 4.95 | 4.97 |
| *ct*-**2b** | 4.11 | 3.64 | 2.90 | 4.04 | 1.87 | 3.05 | 3.54 | 4.26 | 4.00 | 4.22 | 4.17 |
| *tt*-**2b** | 3.18 | 3.51 | 4.70 | 4.83 | 0.61 | 3.38 | 3.36 | 3.29 | 3.03 | 3.38 | 3.24 |
| *cc*-**3b** | 4.80 | 3.89 | 1.32 | 8.70 | 5.86 | 2.89 | 3.85 | 4.97 | 4.23 | 4.80 | 4.86 |
| *ct*-**3b** | 3.98 | 3.54 | 3.39 | 6.15 | 3.68 | 2.85 | 3.19 | 4.07 | 3.90 | 4.09 | 4.03 |
| *tt*-**3b** | 3.09 | 3.21 | 5.63 | 7.24 | 2.01 | 2.86 | 2.42 | 3.12 | 3.65 | 3.34 | 3.12 |
| *cc*-**4b** | 1.94 | 3.04 | 1.36 | 0.92 | 4.57 | 1.68 | 1.90 | 2.04 | 1.62 | 2.06 | 1.98 |
| *ct*-**4b** | 4.33 | 3.77 | 3.19 | 1.16 | 2.27 | 3.47 | 3.68 | 4.45 | 4.27 | 4.45 | 4.39 |
| *tt*-**4b** | 6.01 | 4.19 | 4.27 | 1.23 | 3.18 | 4.81 | 4.98 | 6.15 | 5.65 | 6.15 | 6.09 |
| *cc*-**5b** | 1.61 | 1.52 | 0.79 | 2.49 | 1.20 | 1.02 | 1.34 | 1.72 | 1.61 | 1.75 | 1.66 |
| *ct*-**5b** | 4.71 | 4.43 | 3.98 | 3.52 | 0.33 | 3.80 | 4.10 | 4.77 | 4.48 | 4.73 | 4.73 |
| *tt*-**5b** | 5.84 | 5.12 | 4.45 | 2.66 | 1.39 | 4.85 | 5.04 | 5.94 | 5.81 | 5.94 | 5.87 |

**Table S3.** Dipole moments (μ in Debyes) calculated using the B3LYP/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1a**–**5a** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Full Density** [a] | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1a** | 4.73 | 4.77 | 7.86 | 5.68 | 16.06 | 3.17 | 4.72 | 4.74 | 4.24 | 4.69 | 4.72 |
| *ct*-**1a** | 3.91 | 3.12 | 5.62 | 4.20 | 9.86 | 2.90 | 3.75 | 3.93 | 3.69 | 3.92 | 3.91 |
| *tt*-**1a** | 2.91 | 1.57 | 2.75 | 2.37 | 1.50 | 2.64 | 2.61 | 2.94 | 1.57 | 1.57 | 2.92 |
| *cc*-**2a** | 4.03 | 2.89 | 1.54 | 2.59 | 5.52 | 1.97 | 3.30 | 4.03 | 3.62 | 2.89 | 4.01 |
| *ct*-**2a** | 3.37 | 2.87 | 4.62 | 4.80 | 6.86 | 2.52 | 3.28 | 3.38 | 3.20 | 3.35 | 3.37 |
| *tt*-**2a** | 2.69 | 2.95 | 7.15 | 9.02 | 8.19 | 3.11 | 3.32 | 2.71 | 2.57 | 2.74 | 2.71 |
| *cc*-**3a** | 3.65 | 2.31 | 0.34 | 5.54 | 2.92 | 2.20 | 3.53 | 3.66 | 2.99 | 3.47 | 3.65 |
| *ct*-**3a** | 3.21 | 2.77 | 4.86 | 6.29 | 6.94 | 2.41 | 2.97 | 3.22 | 2.94 | 3.19 | 3.21 |
| *tt*-**3a** | 2.81 | 3.23 | 8.17 | 11.67 | 10.26 | 2.67 | 2.49 | 2.81 | 2.92 | 2.91 | 2.80 |
| *cc*-**4a** | 0.41 | 1.81 | 2.15 | 1.63 | 9.35 | 0.39 | 0.95 | 0.43 | 0.31 | 0.44 | 0.42 |
| *ct*-**4a** | 3.31 | 2.70 | 4.54 | 3.66 | 7.69 | 2.63 | 3.15 | 3.35 | 3.22 | 3.32 | 3.33 |
| *tt*-**4a** | 5.31 | 3.31 | 6.36 | 5.21 | 6.07 | 4.26 | 4.77 | 5.35 | 5.14 | 5.31 | 5.33 |
| *cc*-**5a** | 0.13 | 0.11 | 1.28 | 0.44 | 6.89 | 0.43 | 0.13 | 0.09 | 0.11 | 0.06 | 0.10 |
| *ct*-**5a** | 3.55 | 3.11 | 4.73 | 4.44 | 6.94 | 2.96 | 3.38 | 3.55 | 3.42 | 3.48 | 3.54 |
| *tt*-**5a** | 5.29 | 4.76 | 6.78 | 6.50 | 7.46 | 4.49 | 5.10 | 5.33 | 5.23 | 5.26 | 5.30 |

[a] Values taken from [1].

**Table S4.** Dipole moments (μ in Debyes) calculated using the B3LYP/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1b**–**5b** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Full Density** [a] | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1b** | 4.69 | 4.57 | 5.25 | 1.19 | 8.25 | 3.13 | 4.31 | 4.75 | 4.57 | 4.70 | 4.72 |
| *ct*-**1b** | 4.09 | 3.30 | 3.40 | 1.00 | 4.56 | 2.96 | 3.48 | 4.16 | 4.03 | 4.21 | 4.13 |
| *tt*-**1b** | 3.35 | 2.42 | 0.68 | 1.28 | 4.84 | 2.85 | 2.57 | 3.45 | 3.43 | 3.49 | 3.41 |
| *cc*-**2b** | 4.13 | 2.91 | 0.76 | 6.51 | 1.70 | 2.03 | 3.04 | 4.21 | 3.49 | 4.13 | 4.16 |
| *ct*-**2b** | 3.62 | 3.17 | 2.76 | 4.27 | 1.08 | 2.63 | 3.09 | 3.70 | 3.46 | 3.68 | 3.66 |
| *tt*-**2b** | 3.08 | 3.48 | 4.50 | 4.62 | 0.87 | 3.19 | 3.16 | 3.16 | 2.84 | 3.21 | 3.12 |
| *cc*-**3b** | 3.80 | 2.41 | 1.86 | 9.25 | 4.01 | 2.09 | 3.06 | 3.90 | 3.21 | 3.78 | 3.85 |
| *ct*-**3b** | 3.46 | 3.05 | 3.36 | 6.42 | 2.82 | 2.39 | 2.68 | 3.53 | 3.38 | 3.53 | 3.49 |
| *tt*-**3b** | 3.17 | 3.72 | 5.46 | 7.08 | 2.82 | 2.77 | 2.34 | 3.22 | 3.61 | 3.35 | 3.19 |
| *cc*-**4b** | 1.54 | 3.13 | 0.86 | 1.32 | 3.55 | 1.22 | 1.45 | 1.60 | 3.13 | 1.62 | 1.57 |
| *ct*-**4b** | 3.96 | 3.48 | 2.92 | 1.11 | 1.64 | 3.11 | 3.31 | 4.04 | 3.84 | 4.04 | 4.00 |
| *tt*-**4b** | 5.66 | 3.76 | 4.08 | 1.43 | 0.69 | 4.47 | 4.65 | 5.75 | 5.20 | 5.74 | 5.71 |
| *cc*-**5b** | 1.23 | 1.00 | 0.33 | 2.86 | 1.13 | 0.62 | 0.94 | 1.30 | 1.17 | 1.32 | 1.27 |
| *ct*-**5b** | 4.44 | 4.08 | 3.90 | 3.59 | 1.12 | 3.60 | 3.90 | 4.49 | 4.16 | 4.43 | 4.46 |
| *tt*-**5b** | 5.62 | 4.84 | 4.38 | 2.57 | 0.69 | 4.66 | 4.86 | 5.69 | 5.47 | 5.66 | 5.63 |

[a] Values taken from [1].

**Table S5.** Dipole moments (μ in Debyes) calculated using the MP2/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1a–5a** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Full Density | Mulliken | NPA | GDMA | AIM | Hirshfeld | CM5 | MKS | CHELP | CHELPG | HLY |
| *cc*-**1a** | 4.39 | 4.03 | 7.25 | 5.75 | 16.53 | 2.80 | 4.35 | 4.40 | 3.92 | 4.36 | 4.39 |
| *ct*-**1a** | 3.60 | 2.81 | 5.12 | 6.19 | 10.02 | 2.58 | 3.43 | 3.61 | 3.39 | 3.62 | 3.60 |
| *tt*-**1a** | 2.65 | 1.60 | 2.43 | 11.43 | 1.14 | 2.40 | 2.37 | 2.68 | 2.62 | 2.67 | 2.66 |
| *cc*-**2a** | 3.71 | 2.49 | 0.87 | 2.95 | 5.80 | 1.66 | 2.99 | 3.72 | 3.31 | 3.63 | 3.69 |
| *ct*-**2a** | 3.10 | 2.63 | 4.29 | 4.71 | 6.91 | 2.26 | 3.01 | 3.12 | 2.95 | 3.09 | 3.10 |
| *tt*-**2a** | 2.50 | 2.75 | 6.98 | 8.88 | 8.02 | 2.88 | 3.10 | 2.49 | 2.38 | 2.53 | 2.51 |
| *cc*-**3a** | 3.40 | 2.55 | 0.21 | 5.37 | 3.56 | 2.07 | 3.40 | 3.49 | 2.77 | 3.26 | 3.41 |
| *ct*-**3a** | 2.96 | 2.55 | 4.57 | 3.90 | 6.91 | 2.15 | 2.73 | 2.98 | 2.72 | 2.95 | 2.96 |
| *tt*-**3a** | 2.57 | 2.50 | 7.92 | 2.11 | 9.79 | 2.28 | 2.10 | 2.51 | 2.67 | 2.65 | 2.56 |
| *cc*-**4a** | 0.07 | 0.70 | 1.62 | 1.31 | 9.75 | 0.05 | 0.61 | 0.14 | 0.02 | 0.11 | 0.08 |
| *ct*-**4a** | 3.11 | 2.43 | 4.17 | 3.44 | 7.81 | 2.42 | 2.92 | 3.15 | 3.03 | 3.11 | 3.13 |
| *tt*-**4a** | 5.08 | 3.51 | 6.02 | 5.01 | 5.91 | 4.03 | 4.55 | 5.10 | 4.91 | 5.08 | 5.10 |
| *cc*-**5a** | 0.57 | 0.71 | 0.72 | 0.86 | 6.98 | 0.85 | 0.29 | 0.51 | 0.74 | 0.50 | 0.54 |
| *ct*-**5a** | 3.45 | 3.26 | 4.47 | 4.38 | 6.98 | 2.87 | 3.27 | 3.42 | 3.31 | 3.38 | 3.44 |
| *tt*-**5a** | 5.11 | 4.72 | 6.47 | 6.34 | 7.47 | 4.30 | 4.90 | 5.13 | 5.05 | 5.08 | 5.12 |

**Table S6.** Dipole moments (μ in Debyes) calculated using the MP2/def2-QZVPP molecular wave functions/electron densities and the partial atomic charges derived from these wave functions/electron densities for the conformers of **1b–5b** from Figure 1.

| Conformer | μ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Full Density | Mulliken | NPA | GDMA | AIM | Hirshfeld | CM5 | MKS | CHELP | CHELPG | HLY |
| *cc*-**1b** | 4.17 | 3.71 | 4.36 | 9.73 | 8.04 | 2.61 | 3.78 | 4.23 | 3.61 | 4.19 | 4.19 |
| *ct*-**1b** | 3.54 | 2.78 | 2.62 | 6.57 | 4.55 | 2.44 | 2.96 | 3.61 | 3.49 | 3.66 | 3.57 |
| *tt*-**1b** | 2.83 | 2.11 | 0.03 | 6.56 | 5.88 | 2.40 | 2.11 | 2.94 | 2.91 | 2.97 | 2.88 |
| *cc*-**2b** | 3.62 | 2.34 | 1.73 | 7.10 | 2.07 | 1.56 | 2.57 | 3.74 | 3.02 | 3.64 | 3.66 |
| *ct*-**2b** | 3.14 | 2.68 | 2.53 | 4.53 | 1.35 | 2.19 | 2.63 | 3.25 | 3.01 | 3.21 | 3.17 |
| *tt*-**2b** | 2.65 | 2.99 | 3.99 | 4.21 | 0.02 | 2.75 | 2.73 | 2.72 | 2.41 | 2.76 | 2.68 |
| *cc*-**3b** | 3.34 | 2.43 | 2.75 | 0.67 | 4.06 | 1.76 | 2.73 | 3.50 | 2.82 | 3.35 | 3.40 |
| *ct*-**3b** | 2.98 | 2.57 | 3.20 | 1.10 | 2.66 | 1.93 | 2.24 | 3.04 | 2.94 | 3.06 | 3.02 |
| *tt*-**3b** | 2.68 | 2.74 | 4.88 | 1.81 | 1.67 | 2.18 | 1.74 | 2.69 | 3.11 | 2.84 | 2.69 |
| *cc*-**4b** | 1.09 | 1.90 | 0.13 | 1.79 | 3.36 | 0.80 | 1.03 | 1.18 | 0.75 | 1.18 | 1.12 |
| *ct*-**4b** | 3.61 | 3.07 | 2.46 | 1.28 | 1.33 | 2.79 | 2.98 | 3.69 | 3.51 | 3.68 | 3.65 |
| *tt*-**4b** | 5.22 | 3.71 | 3.45 | 1.00 | 1.51 | 4.08 | 4.26 | 5.33 | 4.77 | 5.30 | 5.27 |
| *cc*-**5b** | 0.67 | 0.40 | 0.49 | 3.46 | 0.64 | 0.08 | 0.40 | 0.75 | 0.61 | 0.75 | 0.71 |
| *ct*-**5b** | 4.23 | 4.15 | 3.70 | 2.65 | 0.88 | 3.43 | 3.71 | 4.26 | 3.96 | 4.20 | 4.24 |
| *tt*-**5b** | 5.24 | 4.64 | 3.76 | 2.19 | 0.05 | 4.30 | 4.49 | 5.32 | 5.09 | 5.28 | 5.25 |

## S2. Selection of a Quantum Chemical Method for Calculating the Reference Full-Density Dipole Moments of 1a–5a and 1b–5b

Since the experimental dipole moments of the gas-phase conformers of **1a–5a** and **1b–5b** from Figure 1 are unknown (to be precise, for some of these compounds their dipole moments were measured experimentally for the mixtures of conformers in various solvents), the reference values of μ are obtained from the full molecular electron densities calculated at the HF/def2-QZVPP, B3LYP/def2-QZVPP and MP2/def2-QZVPP levels of theory. As a result, three sets of reference μ values are obtained and these sets are used for calculating the MSE and RMSE whose values are presented in Figure 3. If a single set of reference μ values is required, it is hard to ascertain whether HF/def2-QZVPP or B3LYP/def2-QZVPP or MP2/def2-QZVPP provides the most reliable full-density values of μ, because the lack of experimental dipole moments for the gas-phase conformers of **1a–5a** and **1b–5b** from Figure 1 makes it impossible. A reasonable solution to this problem is to consider a test set of some other molecules for which the dipole moments were measured experimentally in the gas phase. In our case such a test set is composed of seven simple molecules that are the building

blocks of **1a–5a** and **1b–5b**. The molecules of formaldehyde, thioformaldehyde, furan, thiophene, selenophene, pyrrole and 1-methylpyrrole are taken into account. Their μ values calculated from the HF/def2-QZVPP, B3LYP/def2-QZVPP and MP2/def2-QZVPP full densities, together with their μ values measured experimentally in the gas phase, are listed in Table S7. Additionally, the MSE and RMSE in the calculated μ values relative to the corresponding experimental data are shown in the last two rows in Table S7. These values of the MSE and RMSE clearly indicate that B3LYP/def2-QZVPP performs best in reproducing the experimental dipole moments of the seven molecules. It can be assumed that this level of theory also provides reliable values of μ for larger molecules possessing structural fragments taken from the seven molecules. Therefore, only the μ values obtained from the B3LYP/def2-QZVPP electron densities of the conformers of **1a–5a** and **1b–5b** from Figure 1 are used as the reference values to determine the MSE and RMSE in Figure 4.

**Table S7.** Calculated and experimental μ values for seven simple molecules. The last two rows give the MSE and RMSE of the calculated μ values from the experimental ones. All values in Debyes.

| Molecule | μ | | | |
|---|---|---|---|---|
| | **HF/def2-QZVPP** | **B3LYP/def2-QZVPP** | **MP2/def2-QZVPP** | **Experiment** |
| Formaldehyde | 2.80 | 2.36 | 2.32 | 2.33 [2] |
| Thioformaldehyde | 2.12 | 1.72 | 1.63 | 1.65 [3] |
| Furan | 0.78 | 0.66 | 0.64 | 0.66 [2] |
| Thiophene | 0.74 | 0.50 | 0.48 | 0.55 [2] |
| Selenophene | 0.76 | 0.37 | 0.40 | 0.39 [4] |
| Pyrrole | 1.87 | 1.86 | 1.88 | 1.84 [2] |
| 1-Methylpyrrole | 2.16 | 2.14 | 2.24 | 2.12 [5] |
| MSE | 0.24 | 0.01 | 0.01 | 0.00 |
| RMSE | 0.30 | 0.04 | 0.06 | 0.00 |

## S3. Additional Tables with the Results of Eelst Calculations

**Table S8.** Relative electron energies ($\Delta E$ in kcal/mol), dipole moments from the full density (μ in Debyes) and relative electrostatic energies ($\Delta E_{elst}$ in kcal/mol) for **1a–5a** from Figure 1 in their three conformations. All results obtained at the HF/def2-QZVPP level of theory.

| Conformer | $\Delta E$ | μ | $\Delta E_{elst}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1a** | 2.01 | 5.24 | 13.94 | 12.91 | 12.52 | 51.43 | 3.86 | 5.75 | 0.00 | 0.00 | 0.00 | 0.00 |
| *ct*-**1a** | 0.00 | 4.26 | 4.32 | 0.39 | 0.86 | 1.36 | 2.03 | 2.18 | 8.15 | 15.64 | 14.23 | 47.75 |
| *tt*-**1a** | 0.88 | 2.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 28.80 | 14.44 | 31.94 | 60.08 |
| *cc*-**2a** | 0.00 | 4.75 | 3.97 | 0.00 | 0.00 | 0.00 | 0.00 | 1.06 | 0.00 | 111.04 | 0.00 | 0.00 |
| *ct*-**2a** | 0.91 | 3.75 | 2.88 | 3.87 | 10.47 | 7.29 | 0.22 | 0.75 | 66.47 | 0.00 | 34.60 | 134.34 |
| *tt*-**2a** | 2.48 | 2.63 | 0.00 | 7.14 | 26.76 | 13.43 | 0.39 | 0.00 | 96.69 | 161.25 | 59.15 | 146.93 |
| *cc*-**3a** | 0.00 | 4.61 | 3.29 | 0.00 | 0.00 | 0.00 | 1.23 | 4.56 | 0.00 | 0.00 | 0.00 | 0.00 |
| *ct*-**3a** | 1.39 | 3.64 | 3.22 | 6.53 | 12.84 | 13.23 | 0.75 | 1.81 | 113.05 | 68.39 | 32.25 | 166.92 |
| *tt*-**3a** | 3.36 | 2.56 | 0.00 | 13.50 | 38.58 | 29.05 | 0.00 | 0.00 | 116.82 | 136.80 | 74.43 | 199.66 |
| *cc*-**4a** | 0.00 | 0.60 | 0.00 | 0.00 | 0.00 | 14.46 | 0.00 | 0.00 | 7.93 | 40.04 | 0.13 | 6.46 |
| *ct*-**4a** | 3.66 | 3.51 | 15.67 | 10.28 | 4.61 | 0.00 | 2.19 | 2.53 | 0.00 | 0.00 | 0.00 | 0.00 |
| *tt*-**4a** | 8.43 | 5.53 | 15.60 | 17.29 | 6.57 | 13.11 | 4.07 | 2.34 | 30.42 | 5.69 | 26.22 | 32.50 |
| *cc*-**5a** | 0.00 | 0.12 | 0.00 | 0.00 | 0.00 | 7.82 | 0.00 | 0.99 | 18.97 | 43.43 | 40.16 | 0.00 |
| *ct*-**5a** | 5.59 | 3.70 | 13.56 | 3.82 | 5.20 | 3.41 | 0.58 | 0.27 | 0.00 | 101.71 | 0.00 | 33.67 |
| *tt*-**5a** | 9.75 | 5.48 | 26.62 | 9.36 | 9.96 | 0.00 | 1.64 | 0.00 | 54.84 | 0.00 | 22.04 | 118.23 |

**Table S9.** Relative electron energies ($\Delta E$ in kcal/mol), dipole moments from the full density (μ in Debyes) and relative electrostatic energies ($\Delta E_{elst}$ in kcal/mol) for **1b–5b** from Figure 1 in their three conformations. All results obtained at the HF/def2-QZVPP level of theory.

| Conformer | $\Delta E$ | μ | $\Delta E_{elst}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1b** | 1.32 | 5.21 | 6.21 | 0.00 | 0.00 | 0.00 | 2.25 | 2.11 | 60.55 | 189.18 | 9.66 | 47.41 |
| *ct*-**1b** | 0.00 | 4.58 | 0.00 | 1.67 | 3.72 | 9.04 | 1.23 | 0.39 | 0.00 | 164.13 | 11.22 | 31.04 |
| *tt*-**1b** | 0.62 | 3.63 | 2.15 | 13.12 | 19.26 | 61.54 | 0.00 | 0.00 | 8.82 | 0.00 | 0.00 | 0.00 |
| *cc*-**2b** | 0.00 | 4.92 | 0.00 | 0.00 | 2.16 | 0.00 | 0.00 | 0.00 | 0.00 | 18.63 | 0.00 | 0.00 |
| *ct*-**2b** | 0.91 | 4.11 | 2.08 | 2.80 | 0.00 | 4.75 | 0.30 | 0.33 | 52.86 | 0.00 | 33.33 | 111.86 |
| *tt*-**2b** | 2.42 | 3.18 | 1.72 | 6.14 | 3.01 | 9.49 | 0.61 | 0.40 | 53.38 | 16.95 | 34.58 | 119.60 |
| *cc*-**3b** | 0.00 | 4.80 | 0.00 | 0.00 | 4.08 | 0.00 | 0.90 | 2.71 | 0.00 | 42.90 | 0.00 | 0.00 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *ct*-**3b** | 1.23 | 3.98 | 2.59 | 4.19 | 0.00 | 2.04 | 0.62 | 0.95 | 78.22 | 39.68 | 41.37 | 146.38 |
| *tt*-**3b** | 3.14 | 3.09 | 2.54 | 9.88 | 7.38 | 6.95 | 0.00 | 0.00 | 97.52 | 0.00 | 59.73 | 169.79 |
| *cc*-**4b** | 0.00 | 1.94 | 1.63 | 0.00 | 3.35 | 0.00 | 0.00 | 3.14 | 0.68 | 47.60 | 0.00 | 33.45 |
| *ct*-**4b** | 3.85 | 4.33 | 7.74 | 4.30 | 0.00 | 23.12 | 1.53 | 3.13 | 11.94 | 0.00 | 9.93 | 40.02 |
| *tt*-**4b** | 8.70 | 6.01 | 0.00 | 5.95 | 11.56 | 78.04 | 2.50 | 0.00 | 0.00 | 35.08 | 27.30 | 0.00 |
| *cc*-**5b** | 0.00 | 1.61 | 0.00 | 0.00 | 3.77 | 0.00 | 0.00 | 0.29 | 136.14 | 32.22 | 45.83 | 210.62 |
| *ct*-**5b** | 2.98 | 4.71 | 10.19 | 4.11 | 2.71 | 0.19 | 1.01 | 0.00 | 49.45 | 41.03 | 12.17 | 123.41 |
| *tt*-**5b** | 4.56 | 5.84 | 16.69 | 4.87 | 0.00 | 17.38 | 1.74 | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table S10.** Relative electron energies ($\Delta E$ in kcal/mol), dipole moments from the full density ($\mu$ in Debyes) and relative electrostatic energies ($\Delta E_{elst}$ in kcal/mol) for **1a–5a** from Figure 1 in their three conformations. All results obtained at the B3LYP/def2-QZVPP level of theory.

| **Conformer** | $\Delta E$ [a] | $\mu$ [b] | $\Delta E_{elst}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1a** | 2.14 | 4.73 | 13.78 | 9.13 | 8.91 | 35.42 | 1.81 | 3.50 | 0.07 | 0.00 | 0.00 | 0.00 |
| *ct*-**1a** | 0.00 | 3.91 | 4.13 | 0.00 | 0.25 | 0.95 | 1.10 | 1.38 | 0.47 | 6.88 | 2.83 | 19.65 |
| *tt*-**1a** | 0.34 | 2.91 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 35.45 | 25.88 | 25.15 |
| *cc*-**2a** | 0.00 | 4.03 | 0.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 94.79 | 93.35 | 0.00 |
| *ct*-**2a** | 0.77 | 3.37 | 0.30 | 5.13 | 10.54 | 5.29 | 0.68 | 0.32 | 44.47 | 0.00 | 0.00 | 64.19 |
| *tt*-**2a** | 1.85 | 2.69 | 0.00 | 10.54 | 27.76 | 10.58 | 1.47 | 0.33 | 50.28 | 146.08 | 11.30 | 69.59 |
| *cc*-**3a** | 0.00 | 3.65 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.07 | 0.00 | 0.00 | 0.00 | 0.00 |
| *ct*-**3a** | 1.41 | 3.21 | 1.01 | 6.72 | 12.43 | 10.11 | 0.15 | 1.02 | 53.46 | 20.77 | 13.24 | 68.89 |
| *tt*-**3a** | 2.93 | 2.81 | 1.42 | 15.42 | 39.39 | 22.96 | 0.05 | 0.00 | 69.25 | 109.74 | 35.93 | 87.14 |
| *cc*-**4a** | 0.00 | 0.41 | 0.00 | 0.00 | 0.00 | 5.38 | 0.00 | 0.00 | 0.00 | 36.85 | 0.85 | 0.00 |
| *ct*-**4a** | 3.82 | 3.31 | 10.99 | 7.20 | 3.95 | 0.00 | 1.75 | 2.05 | 6.79 | 0.00 | 0.00 | 1.51 |
| *tt*-**4a** | 8.99 | 5.31 | 9.77 | 10.97 | 5.57 | 8.28 | 3.34 | 1.37 | 26.92 | 8.62 | 19.90 | 25.70 |
| *cc*-**5a** | 0.00 | 0.13 | 0.00 | 0.00 | 0.00 | 3.35 | 0.00 | 0.93 | 0.00 | 90.53 | 29.48 | 0.00 |
| *ct*-**5a** | 5.37 | 3.55 | 8.00 | 1.44 | 4.43 | 3.30 | 0.50 | 0.41 | 36.19 | 80.44 | 0.00 | 44.15 |
| *tt*-**5a** | 9.63 | 5.29 | 28.21 | 5.27 | 8.35 | 0.00 | 1.36 | 0.00 | 99.21 | 0.00 | 16.44 | 106.26 |

[a] Values taken from [6];[b] Values taken from [1].

**Table S11.** Relative electron energies (Δ*E* in kcal/mol), dipole moments from the full density (μ in Debyes) and relative electrostatic energies (Δ$E_{elst}$ in kcal/mol) for **1b–5b** from Figure 1 in their three conformations. All results obtained at the B3LYP/def2-QZVPP level of theory.

| Conformer | Δ*E* [a] | μ [b] | Δ$E_{elst}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mulliken | NPA | GDMA | AIM | Hirshfeld | CM5 | MKS | CHELP | CHELPG | HLY |
| *cc*-**1b** | 1.46 | 4.69 | 7.79 | 0.00 | 0.00 | 0.00 | 0.80 | 0.95 | 51.02 | 142.69 | 14.85 | 42.63 |
| *ct*-**1b** | 0.00 | 4.09 | 0.00 | 0.60 | 3.30 | 2.22 | 0.62 | 0.13 | 10.35 | 134.71 | 9.03 | 11.94 |
| *tt*-**1b** | 0.31 | 3.35 | 0.75 | 9.21 | 16.12 | 36.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *cc*-**2b** | 0.00 | 4.13 | 0.00 | 0.00 | 3.06 | 0.00 | 0.00 | 0.00 | 0.00 | 21.19 | 0.00 | 0.00 |
| *ct*-**2b** | 0.99 | 3.62 | 1.02 | 2.81 | 0.00 | 2.09 | 0.48 | 0.53 | 37.25 | 0.00 | 11.95 | 49.47 |
| *tt*-**2b** | 2.22 | 3.08 | 1.23 | 5.97 | 3.04 | 4.48 | 1.15 | 0.95 | 35.82 | 36.44 | 8.01 | 51.96 |
| *cc*-**3b** | 0.00 | 3.80 | 0.00 | 0.00 | 5.46 | 0.00 | 0.25 | 2.18 | 0.00 | 6.28 | 0.00 | 0.00 |
| *ct*-**3b** | 1.44 | 3.46 | 2.09 | 3.19 | 0.00 | 1.51 | 0.27 | 0.63 | 56.32 | 25.36 | 15.35 | 57.83 |
| *tt*-**3b** | 3.00 | 3.17 | 3.05 | 8.09 | 7.57 | 5.66 | 0.00 | 0.00 | 65.31 | 0.00 | 20.18 | 67.72 |
| *cc*-**4b** | 0.00 | 1.54 | 0.64 | 0.61 | 9.19 | 0.00 | 0.00 | 3.74 | 27.94 | 0.00 | 0.00 | 31.98 |
| *ct*-**4b** | 3.92 | 3.96 | 5.86 | 1.76 | 5.52 | 11.12 | 1.22 | 3.52 | 37.82 | 3.33 | 6.97 | 41.82 |
| *tt*-**4b** | 9.41 | 5.66 | 0.00 | 0.00 | 0.00 | 38.50 | 1.95 | 0.00 | 0.00 | 27.77 | 15.71 | 0.00 |
| *cc*-**5b** | 0.00 | 1.23 | 0.00 | 0.00 | 3.70 | 0.00 | 0.00 | 0.18 | 180.49 | 25.54 | 36.69 | 180.68 |
| *ct*-**5b** | 3.05 | 4.44 | 10.21 | 2.39 | 2.54 | 0.01 | 0.91 | 0.00 | 117.01 | 34.11 | 13.65 | 113.67 |
| *tt*-**5b** | 5.04 | 5.62 | 17.64 | 2.19 | 0.00 | 7.42 | 1.60 | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 |

[a] Values taken from [6]; [b] Values taken from [1].

**Table S12.** Relative electron energies (Δ*E* in kcal/mol), dipole moments from the full density (μ in Debyes) and relative electrostatic energies (Δ$E_{elst}$ in kcal/mol) for **1a–5a** from Figure 1 in their three conformations. All results obtained at the MP2/def2-QZVPP level of theory.

| Conformer | Δ*E* | μ | Δ$E_{elst}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Mulliken | NPA | GDMA | AIM | Hirshfeld | CM5 | MKS | CHELP | CHELPG | HLY |
| *cc*-**1a** | 1.29 | 4.39 | 7.20 | 7.39 | 7.95 | 35.06 | 1.22 | 2.74 | 7.80 | 3.80 | 0.00 | 0.00 |
| *ct*-**1a** | 0.00 | 3.60 | 2.08 | 0.00 | 0.00 | 0.00 | 0.79 | 1.02 | 0.00 | 0.00 | 2.25 | 16.81 |
| *tt*-**1a** | 0.41 | 2.65 | 0.00 | 1.60 | 0.29 | 1.30 | 0.00 | 0.00 | 10.67 | 12.67 | 8.79 | 20.76 |
| *cc*-**2a** | 0.00 | 3.71 | 0.60 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 76.66 | 0.00 | 0.00 |
| *ct*-**2a** | 0.81 | 3.10 | 1.11 | 5.57 | 10.24 | 4.28 | 0.66 | 0.34 | 18.05 | 0.00 | 12.75 | 50.74 |
| *tt*-**2a** | 1.51 | 2.50 | 0.00 | 11.46 | 27.61 | 8.14 | 1.48 | 0.40 | 30.62 | 136.71 | 22.00 | 57.09 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *cc*-**3a** | 0.00 | 3.40 | 0.57 | 0.00 | 0.00 | 0.00 | 0.25 | 3.28 | 0.00 | 0.00 | 0.00 | 0.00 |
| *ct*-**3a** | 1.20 | 2.96 | 1.46 | 7.03 | 11.78 | 7.65 | 0.24 | 1.13 | 25.15 | 26.77 | 10.72 | 50.31 |
| *tt*-**3a** | 2.12 | 2.57 | 0.00 | 15.69 | 37.93 | 16.94 | 0.00 | 0.00 | 17.49 | 107.68 | 28.46 | 67.53 |
| *cc*-**4a** | 0.00 | 0.07 | 0.00 | 0.00 | 0.00 | 7.21 | 0.00 | 0.00 | 0.00 | 32.18 | 0.00 | 0.00 |
| *ct*-**4a** | 3.48 | 3.11 | 10.46 | 6.70 | 3.88 | 0.00 | 1.69 | 2.11 | 2.84 | 0.00 | 0.68 | 6.79 |
| *tt*-**4a** | 8.60 | 5.08 | 7.23 | 9.81 | 5.38 | 9.26 | 3.23 | 1.40 | 23.45 | 6.04 | 20.18 | 26.32 |
| *cc*-**5a** | 0.00 | 0.57 | 0.00 | 0.00 | 0.00 | 3.59 | 0.00 | 0.83 | 24.23 | 37.43 | 31.81 | 0.00 |
| *ct*-**5a** | 4.54 | 3.45 | 10.02 | 1.23 | 4.23 | 2.65 | 0.46 | 0.39 | 0.00 | 90.75 | 0.00 | 44.26 |
| *tt*-**5a** | 7.59 | 5.11 | 18.93 | 3.98 | 7.92 | 0.00 | 1.24 | 0.00 | 52.42 | 0.00 | 15.32 | 101.37 |

**Table S13.** Relative electron energies ($\Delta E$ in kcal/mol), dipole moments from the full density (μ in Debyes) and relative electrostatic energies ($\Delta E_{elst}$ in kcal/mol) for **1b**–**5b** from Figure 1 in their three conformations. All results obtained at the MP2/def2-QZVPP level of theory.

| **Conformer** | **$\Delta E$** | **μ** | **$\Delta E_{elst}$** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Mulliken** | **NPA** | **GDMA** | **AIM** | **Hirshfeld** | **CM5** | **MKS** | **CHELP** | **CHELPG** | **HLY** |
| *cc*-**1b** | 0.40 | 4.17 | 2.84 | 0.00 | 0.00 | 0.00 | 0.40 | 0.63 | 69.81 | 161.55 | 20.11 | 47.08 |
| *ct*-**1b** | 0.00 | 3.54 | 0.00 | 1.05 | 3.14 | 5.30 | 0.39 | 0.00 | 0.00 | 148.13 | 11.77 | 12.40 |
| *tt*-**1b** | 0.62 | 2.83 | 2.40 | 10.93 | 16.02 | 45.35 | 0.00 | 0.11 | 15.88 | 0.00 | 0.00 | 0.00 |
| *cc*-**2b** | 0.00 | 3.62 | 0.00 | 0.00 | 4.16 | 0.00 | 0.00 | 0.00 | 62.83 | 16.08 | 0.34 | 0.00 |
| *ct*-**2b** | 1.15 | 3.14 | 3.34 | 1.97 | 0.00 | 1.52 | 0.41 | 0.48 | 3.80 | 0.00 | 6.20 | 36.07 |
| *tt*-**2b** | 2.25 | 2.65 | 3.88 | 4.56 | 2.34 | 3.23 | 1.08 | 0.90 | 0.00 | 34.68 | 0.00 | 36.91 |
| *cc*-**3b** | 0.00 | 3.34 | 0.00 | 0.00 | 6.60 | 0.00 | 0.30 | 2.10 | 0.00 | 0.09 | 0.00 | 0.00 |
| *ct*-**3b** | 1.41 | 2.98 | 3.40 | 2.20 | 0.00 | 0.35 | 0.28 | 0.59 | 8.93 | 30.38 | 9.32 | 42.15 |
| *tt*-**3b** | 2.69 | 2.68 | 4.09 | 5.94 | 6.19 | 2.63 | 0.00 | 0.00 | 9.40 | 0.00 | 10.02 | 48.09 |
| *cc*-**4b** | 0.00 | 1.09 | 3.15 | 3.60 | 10.64 | 0.00 | 0.00 | 3.56 | 2.68 | 32.81 | 0.00 | 33.73 |
| *ct*-**4b** | 3.65 | 3.61 | 7.68 | 3.59 | 6.27 | 10.93 | 1.23 | 3.48 | 25.56 | 0.00 | 9.20 | 49.17 |
| *tt*-**4b** | 9.07 | 5.22 | 0.00 | 0.00 | 0.00 | 40.99 | 1.96 | 0.00 | 0.00 | 20.82 | 18.04 | 0.00 |
| *cc*-**5b** | 0.00 | 0.67 | 0.00 | 0.00 | 4.64 | 0.00 | 0.00 | 0.03 | 119.65 | 31.20 | 44.73 | 195.95 |
| *ct*-**5b** | 2.48 | 4.23 | 9.31 | 1.17 | 6.96 | 0.46 | 0.93 | 0.00 | 70.21 | 31.51 | 18.08 | 128.64 |
| *tt*-**5b** | 3.11 | 5.24 | 13.88 | 1.60 | 0.00 | 9.66 | 1.59 | 0.19 | 0.00 | 0.00 | 0.00 | 0.00 |

## References

1. Matczak, P.; Domagała, M. Charge distribution in conformers of diheteroaryl ketones and thioketones. Submitted.
2. Nelson, R.D., Jr.; Lide, D.R., Jr.; Maryott, A.A. *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*; U.S. National Bureau of Standards: Washington, DC, USA, 1967.
3. Hellwege, K.H.; Hellwege, A.M. *Molecular Constants from Microwave, Molecular Beam, and Electron Spin Resonance Spectroscopy*; Springer-Verlag: Berlin, Germany, 1974.
4. Fringuelli, F.; Marino, G.; Taticchi, A. Tellurophene and Related Compounds. *Adv. Heterocycl. Chem.* **1977**, *21*, 119–173.
5. Arnold, W.; Dreizler, H.; Rudolph, H.D. Mikrowellenspektrum, hinderungspotential der internen rotation, dipolmoment und quadrupolkopplungskonstanten des n-methylpyrrols. *Z. Naturforsch. A* **1968**, *23*, 301–306.
6. Matczak, P.; Domagała, M.; Domagała, S. Conformers of diheteroaryl ketones and thioketones: A quantum chemical study of their properties and fundamental intramolecular energetic effects. *Struct. Chem.* **2015**, doi:10.1007/s11224-015-0643-3.