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Reduction potential of β-diketones: Effect of electron donating, aromatic and ester substituent groups

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An electrochemical and computational chemistry study of selected β-diketones is presented. The effect of electron donating, aromatic and ester groups on the 1 and 3 position of the β-diketones, on the reduction potential of β-diketones, is illustrated and discussed. An analysis of the density functional theory (DFT) calculated spin density profile and molecular electrostatic potential of the reduced β-diketone, gives insight into the electron distribution in the reduced molecule. DFT calculated lowest unoccupied molecular orbital energies (E_{LUMO}) of the β-diketone relate linearly to the experimental reduction potential. This result could be used to determine the expected experimental reduction potential of newly designed β-diketones.

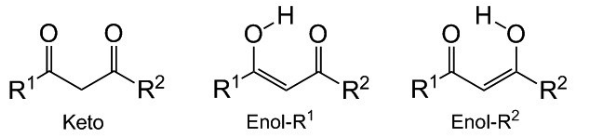
Keywords: beta-diketone; reduction potential; experimental-DFT relationships, oligothiophene

Reduksiepotensiaal van β-diketone: Die effek van elektronskenkende, aromatiese en estersubstituentgroepe: ʼn Elektrochemiese en berekeningschemiese studie van geselekteerde β-diketone word aangebied. Die effek van elektronskenkende, aromatiese en estergroepe op die 1 en 3 posisie van die β-diketone op die reduksiepotensiaal van β-diketone word geïllustreer en bespreek. ʼn Analise van die digtheidfunksionaalteorie-berekende (DFT-berekende) spin digtheidsprofiel en molekulêre elektrostatiese potensiaal van die gereduseerde β-diketone gee insig in die elektronverspreiding in die gereduseerde molekule. Daar is bevind dat die digtheidfunksionaalteorie-berekende (DFT-berekende) laagste ongevulde molekulêre orbitaal energieë (E_{LOMO}) van die β-diketoon lineêr verband hou met die eksperimentele reduksiepotensiaal. Hierdie resultaat kan gebruik word om die verwagte eksperimentele reduksiepotensiaal van nuut-ontwerpte β-diketone te bepaal.

Sleutelwoorde: beta-diketoon; reduksiepotensiaal; eksperimentele-DFT verwantskappe, oligotiofeen

Introduction

A β-diketone (1,3-substituted-propane-1,3-dione), $R^1COCHC(OH)R^2$, typically acts as bidentate ligand with two oxygen donor atoms. It is a tautomeric molecule, existing as a mixture of keto and enol isomers in equilibrium with each other, with the enol, the predominantly main form, in solution (Conradie et al. 2008). β-diketones are important organic reagents (Katritzky et al. 2004) and excellent chelates for transition metals (Stary 1964), rare earth metals (Gschneidner Jr et al. 2005) and actinide ions (Vigato et al. 2009). For all of these applications a knowledge of the stability of the β-diketone towards deprotonation and reduction, is important. The experimental reduction potential of a series of ten β-diketones, $R^1COCHC(OH)R^2$, **1 – 9** and **11**, as shown in Figure 1, with different substituent groups R^1 and R^2 on the β-diketone, has been reported (Kuhn et al. 2011). The reported reduction potentials vary over a range of 1.1 V between -1.05 and -2.14 V *vs* FcH/FcH$^+$ (where FcH = Ferrocene). This paper aims to expand the previous study to (i) increase the reported range of reduction potentials of these β-diketones (Figure 1), (ii) provide relationships between the experimental reduction potentials of these β-diketones and DFT calculated energies, and (iii) illustrate the influence of electron-donating, electron-withdrawing, aromatic and ester groups on the reduction potentials of a series of β-diketones.



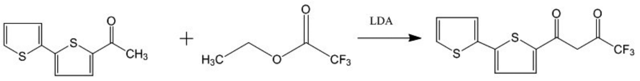
	R^1	R^2		R^1	R^2		R^1	R^2
1.	CF_3	*p*-C_6H_4-NO_2	**6.**	CF_3	$C(CH_3)_3$	**11.**	Ph	CH_3
2.	CF_3	CF_3	**7.**	Th	Th	**12.**	$C(CH_3)_3$	$C(CH_3)_3$
3.	CF_3	Th	**8.**	Ph	Th	**13.**	CH_3	OCH_3
4.	CF_3	Ph	**9.**	Ph	Ph	**14.**	CF_3	C_4H_2S-Th
5.	CF_3	CH_3	**10.**	CH_3	CH_3	**15.**	CF_3	Fu

FIGURE 1: The isomeric forms and numbering of the β-diketones used in this study. Th = C_4H_3S, Ph = C_6H_5, Fu = C_4H_3O.

Material and methods

Synthesis

The thiophene β-diketones 7 and 8 were synthesised and characterised as described in literature (Conradie et al. 2008), while β-diketone **14** was synthesised from 5-acetyl-2,2′-bithiophene as described in Scheme 1. The other β-diketones (Sigma-Aldrich) were used as received, without further purification.



SCHEME 1: Synthesis of 1-[2,2′-bithiophen]-5-yl-4,4,4-trifluoro-1,3-butanedione, **14**, from 5-acetyl-2,2′-bithiophene and ethyl trifluoroacetate

5-Acetyl-2,2′-bithiophene

2,2′-Bithiophene (1.024 g, 6 mmol) was mixed with acetic anhydride (1.234 g, 12 mmol) and zinc chloride (0.0245 g, 0.18 mmol). The dark green solution was refluxed for a period of four hours. After cooling, water (40 mL) was added to the solid brown material. Diethyl ether was added and the precipitate was crushed until fine and then extensively washed with diethyl ether. The remaining precipitate is the byproduct, preliminarily assigned to $(CH_3CO)_2(C_4H_3S)_2$, according to the ^{1}H NMR spectrum. The filtrate containing the desired product was neutralised with sodium carbonate solution (0.05 M). The organic layer was washed with water (3 x 50 mL) and dried with magnesium sulfate. The magnesium sulfate was filtered off and the solvent was removed under reduced pressure, resulting in an orange precipitate. The orange precipitate was washed with methanol to remove the unreacted starting material. The solvent was removed under reduced pressure. Spectroscopically pure 5-acetyl-2,2′-bithiophene (orange powder) was obtained (0.538 g, 42% yield). δ_H (300 MHz, $CDCl_3$): 2.551 (3H, s, CH_3), 7.061 (1H, dd, ^3J = 4 Hz, ^3J = 5 Hz, CH), 7.174 (1H, d, ^3J = 4 Hz, CH), 7.336 – 7.314 (2H, m, CH), 7.589 (1H, d, ^3J = 4 Hz, CH).

1-[2,2′-Bithiophen]-5-yl-4,4,4-trifluoro-1,3-butanedione, 14

β-diketone **14** was synthesised under Schlenk conditions. The system was flame dried and degassed under Argon gas. An argon atmosphere was maintained throughout the reaction. 5-Acetyl-2,2′-bithiophene (2.000 g, 9.6 mmol) was dissolved in THF (15 mL) and left to stir for a few minutes. Lithium diisopropylamide, LDA (5 mL of 2.0 M solution in THF/heptane/ethylbenzene, 10 mmol) was slowly added to the solution, kept on an ice bath and allowed to stir at 0 °C for 15 minutes. Ethyl trifluoroacetate (1.2 mL, 10.0 mmol) was added to the orange solution. The reaction mixture was left to stir at room temperature for 24 hours. The dark brown solution was acidified with HCl (100 mL, 0.3 M) and extracted with diethyl ether (2 x 50 mL). The organic layer was thoroughly washed with water (2 x 100 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure. Spectroscopically pure 1-[2,2′-bithiophen]-5-yl-4,4,4-trifluoro-1,3-butanedione was obtained (2.559 g, 87.6%). δ_H (300 MHz, $CDCl_3$): 6.415 (1H, s, CH), 7.090 (1H, dd, ^3J = 4 Hz, ^3J = 5 Hz, CH), 7.242 (1H, d, ^3J = 4 Hz, CH), 7.366 – 7.391 (2H, m, CH), 7.737 (1H, d, ^3J = 4 Hz, CH).

Theoretical calculations

DFT calculations were performed using (i) the B3LYP functional with the triple-ζ basis set 6-311G(d,p) as implemented in the Gaussian 16 package (Frisch et al. 2016), and (ii) the OLYP functional with the all electron TZP (Triple ζ polarised) basis set as implemented in the Amsterdam Density Functional program (ADF2018) (Te Velde et al. 2001). Frequency analysis was done on all compounds to confirm that the optimised structures did not exhibit any imaginary frequencies, thus all are real minimum energy structures. Calculations were done in the gas phase, as well as the experimental solvent of the electrochemical study, CH_3CN. For the solvent calculations utilising Gaussian 16, the solvation model density (SMD) (Marenich et al. 2009) polarisable continuum model (PCM) was used, with an integral equation formalism variant (IEF-PCM) (Skeyner et al. 2015). For the solvent calculations utilising ADF, the COSMO (Conductor like Screening Model) model of solvation (Klamt and Schüürmann 1993; Klamt 1995; Klamt and Jones 1996) is implemented. When comparing experimental and calculated data of compounds **1**, **3 – 6**, **11**, **13 – 15** an effective calculated energy was determined by using the ratio of the relative population of the two enol isomers, as determined by the Boltzmann equation.

To predict reactive sites for electrophilic and nucleophilic attacks for the compounds, a Molecular Electrostatic Potential, MESP surface was simulated from the optimised B3LYP geometries, using the chelp (charges from electrostatic potential) keyword in Gaussian 16. The MESP, V(*r*) at a point *r*, was calculated using the standard equation,

$$V(r) = \sum_{A}^{N} \frac{Z_A}{|r - R_A|} - \frac{\rho(r')d^3r'}{|r - r'|}$$

where the summation runs over all the nuclei A in the compound. Z_A is the charge on the nucleus A at position R_A; $\rho(r')$ is the electron density; and N is the total number of nuclei (Gadre and Shirsat 2000).

Electrochemistry

Electrochemical studies by means of cyclic voltammetry (CV) were performed on 0.002 M or on saturated compound solutions of the complexes in dry acetonitrile, containing 0.1 M tetra-*n*-butylammoniumhexafluorophosphate ([^{n}Bu$_4$N][PF$_6$]) as supporting electrolyte, under a blanket of purified argon, at 25 °C, utilising a BAS 100B/W electrochemical analyser. A three-electrode cell was used, with a glassy carbon (surface area 7.07 x 10^{-6} m^2) working electrode, Pt auxiliary electrode and a Ag/Ag$^+$ (0.010 M AgNO$_3$ in CH$_3$CN) reference electrode (Sawyer and Roberts 1974), mounted on a Luggin capillary (Evans et al. 1983). Scan rates for the CVs were 0.05–5.00 V s^{-1}. Successive experiments under the same experimental conditions showed that all oxidation and reduction potentials were reproducible within 0.010 V. All cited potentials were referenced against the FcH/FcH$^+$ couple, as suggested by IUPAC (Gritzner and Kuta 1984). Ferrocene (FcH) exhibited a peak separation of $\Delta E_p = E_{pa} - E_{pc} = 0.070$ V and peak current ratio $i_{pc}/i_{pa} = 1.00$ under our experimental conditions (pa = peak anodic and pc = peak cathodic).

Results and discussion

Electrochemistry

The cyclic voltammograms (CVs) of β-diketones (CH$_3$COCHC(OH)CH$_3$) **10**, (C(CH$_3$)$_3$COCHC(OH)C(CH$_3$)$_3$) **12** and (CH$_3$COCHC(OH)(OCH$_3$)) **13** are shown in Figure 2. The experimental reduction potential at a scan rate of 0.100 V s^{-1}, as obtained from the CVs, are presented in Table 1, together with previously reported reduction potentials of β-diketones, obtained under the same experimental conditions. The results show that by introducing the electron-donating groups CH$_3$ or C(CH$_3$)$_3$ on the β-diketones **10** and **12**, the experimental reduction potential shifted to more negative values, namely to -2.618 and -2.748 V vs FcH/FcH$^+$ respectively. However, introduction of the ester group OCH$_3$ on the β-diketone **13**, led to an even more negative experimental reduction potential of -3.017 V vs FcH/FcH$^+$. These reduction values are up to 0.9 V more negative than the most negative value of the reported reduction values on a series of β-diketones (Kuhn et al. 2011) that ranged between -1.05 and -2.14 V vs FcH/FcH$^+$. The reduction potential obtained for (CH$_3$COCHC(OH)CH$_3$) **10**, -2.618 V vs FcH/FcH$^+$, is in agreement with a published result of -2.20 V vs SCE in CH$_3$CN (Neal and Murray 1970) which is -2.62 V vs FcH/FcH$^+$ (Pombeiro 2005).

The CVs of the β-diketones **10**, **12** and **13** are chemically and electrochemically irreversible, as expected, due to the instability of the radical anion that forms upon reduction (Buchta and Evans 1970; Buchta and Evans 1968). However, it has been observed that CVs of β-diketones R^{1}COCHC(OH)R^2 of which both the substituent groups R^1 and R^2 are aromatic, showed a re-oxidation peak, only at higher scan rates. Two aromatic substituents in the 1 and 3 position respectively, chemically stabilise the radical anion that forms upon reduction, on the time scale of CVs at high scan rates (> 2 V s^{-1}) (Kuhn et al. 2011; Buchta and Evans 1968). In Figure 3, the CVs of β-diketones (ThCOCHC(OH)Th) **7** and (ThCOCHC(OH)Ph) **8**, each containing two aromatic substituents, are compared with the CV of (CF$_3$COCHC(OH)(C$_4$H$_2$S-Th)) **14**, containing two joined aromatic thienyl groups in the one substituent position.

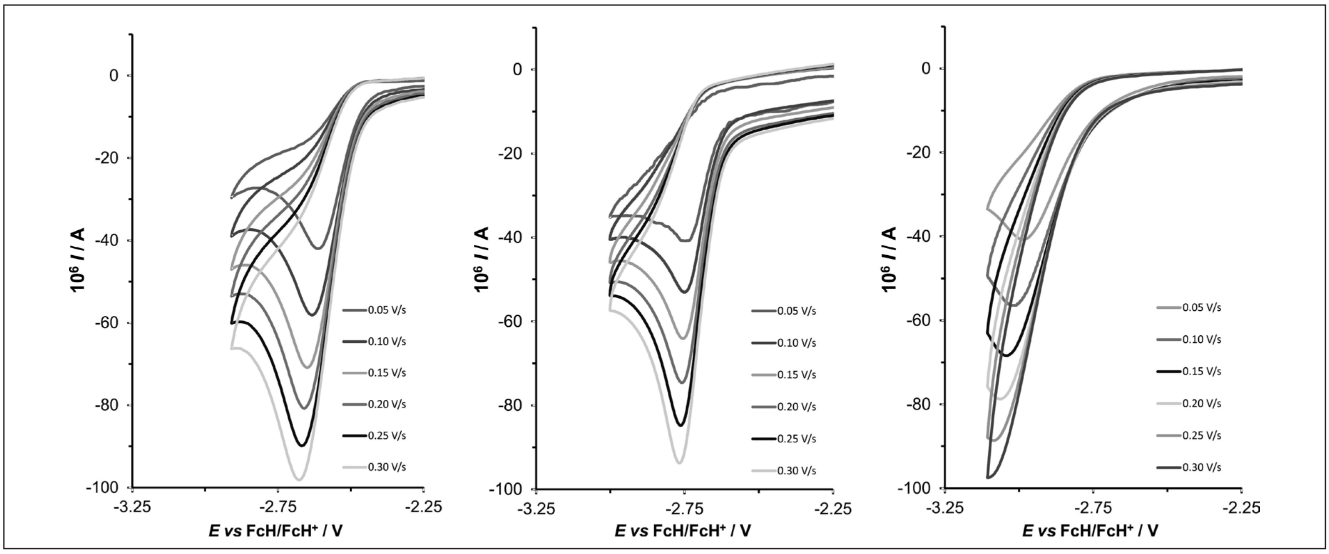


FIGURE 2. Cyclic voltammograms (*vs* FcH/FcH$^+$) at the indicated scan rates (V s^{-1}) for β-diketones (CH$_3$COCHC(OH)CH$_3$) **10** (left), (C(CH$_3$)$_3$COCHC(OH)C(CH$_3$)$_3$) **12** (middle) and (CH$_3$COCHC(OH)(OCH$_3$)) **13** (right), at 25 °C. Solvent/electrolyte = 0.1 M [^{n}Bu$_4$N][PF$_6$]/CH$_3$CN.

We observe that the two joined aromatic groups in the one substituent position, did not lead to any chemically reversible behaviour at higher scan rates. The reduction potential of ($CF_3COCHC(OH)(C_4H_2S$-Th)) **14**, (-1.470 V *vs* FcH/FcH$^+$) containing two joined thienyl groups, is slightly more positive than the reduction potential of ($CF_3COCHC(OH)Th$) **3**, (-1.541 V vs FcH/FcH$^+$), containing only one thienyl group.

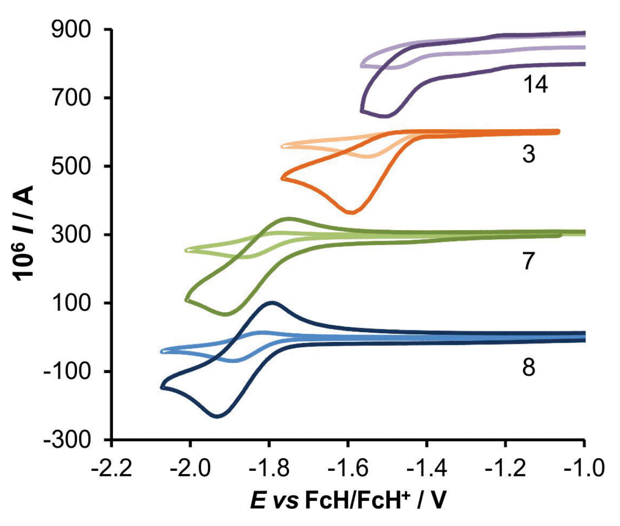


FIGURE 3: Cyclic voltammograms (vs FcH/FcH+) for oligothiophene β-diketones ($CF_3COCHC(OH)(C_4H_2S$-Th) **14**, ($CF_3COCHC(OH)Th$) **3**, ($ThCOCHC(OH)Th$) **7** and ($ThCOCHC(OH)Ph$) **8**, at scan rates 0.20 and 2.00 V s^{-1}, at 25 °C. Solvent/electrolyte = 0.1 M [$^nBu_4N$][PF_6]/CH_3CN.

Effect of electron-donating and aromatic groups

The R side groups (R^1 and R^2) on the β-diketones, $R^1COCHC(OH)R^2$, **1 – 15**, have different electron-donating (or electron-withdrawing) properties due to inductive (CF_3 and aliphatic groups) or resonance effects. The resonance effect includes electron donation from aromatic groups (phenyl, thienyl or furyl) or from a lone-pair of electrons (on O of ester group OCH_3). Empirical parameters that are used to quantify the electron-donating property of the R groups, are Gordy scale group electronegativities, χ_R, (Wells 1968, Kagarise 1955) and Hammett meta substituent constants, $\sigma_{meta,R}$ (McDaniel and Brown 1958, Hammett 1935, Hammett 1937, Hansch et al. 1991). Due to good communication (via induction and resonance) between the R groups and the β-diketonato backbone, the electronic effect of each group on the β-diketone is additive, thus the sum total of the electronegativities ($\chi_{R1} + \chi_{R2}$) and Hammett meta substituent constants ($\sigma_{R1} + \sigma_{R2}$) is used. The influence of the different R^1 and R^2 groups on the reduction potential of β-diketones, $R^1COCHC(OH)R^2$, **1 – 15**, is illustrated in Figure 4 with the data given in Table 1. When considering complexes **2**, **5**, **6**, **10** and **12** of which the aliphatic R groups exhibit a pure σ inductive effect, linear relationships are obtained between the reduction potential and accumulating electron-donating (or electron-withdrawing) effect when expressed as ($\sigma_{R1} + \sigma_{R2}$) or ($\chi_{R1} + \chi_{R2}$) of the R groups involved, R = CH_3, $C(CH_3)_3$ or CF_3. The reduction potential of β-diketone **12** containing two strongly electron-donating $C(CH_3)_3$ groups is 1.5 V more negative than the reduction potential of β-diketone **2** (containing two strongly electron-withdrawing CF_3 groups). Similarly, the reduction potential of β-diketone **5** (containing only one strongly electron-withdrawing CF_3 group) is 0.6 V more negative than that of β-diketone **2**. However, the effect of an aromatic R group on the reduction potential of β-diketones is an interplay of the inductive effect through the σ-system and a resonance effect through the π-system (also see the lowest unoccupied molecular orbital in Figure 7 and the related discussion in the next section). The resonance effect leads to a less negative reduction potential than expected (compound is more easily reduced) if only inductive effects are present. The data points of all the β-diketones **1**, **3**, **4**, **7**, **8**, **9**, **11**, **14** and **15**, (indicated with red crosses) in Figure 4, containing at least one aromatic group, lie above the trend line – showing the pure inductive effect of the R groups on the reduction potential. This implies that the stabilisation of electron density of the neutral β-diketone through resonance, leads to a higher electron affinity of the neutral β-diketone to take up an electron (to be reduced). Deviation of aromatic-group-containing β-diketones from the trend line showing the pure inductive effect in Figure 4 (left) when considering the (Gordy scale) group electronegativities, is larger, because this parameter relies solely on inductive electron withdrawing effects of the substituents. However, electron donation *via* lone pair resonance (on the O of the ester group OCH_3 in β-diketone **13**) leads to a more negative reduction potential than expected from a pure inductive effect (blue triangle in Figure 4). The effect of electron donation via lone pair resonance is thus to stabilise the neutral β-diketone, increasing the electron density on the backbone of the β-diketone, making it more difficult to be reduced at a lower potential (lower electron affinity), see Figure 5.

DFT results

Figure 4 indicates a clear trend between the electron-donating power of the R side groups (R^1 and R^2) on the β-diketones, $R^1COCHC(OH)R^2$, **1 – 15**, and the reduction potential E_{pc} of the β-diketones. However, aromatic and ester groups lead to a deviation of the linear relationship obtained if only β-diketones with aliphatic and CF_3 groups, exhibiting a pure inductive effect, are considered. The combined inductive and resonance effect of the R side groups in **1 – 15** on the reduction potential E_{pc}, can, however, be determined theoretically, using density functional theory calculated energies. Figure 6 illustrates the quite well-defined linear relationship obtained between the reduction potential E_{pc} of the β-diketones **1 – 15**, and density functional theory (DFT) calculated energies of the lowest unoccupied molecular orbital (E_{LUMO}) (R^2 = 0.97 for gas phase calculations using the generalised gradient approximation (GGA) OLYP functional, and 0.98 for calculations using CH_3CN as a solvent). There exists a clear

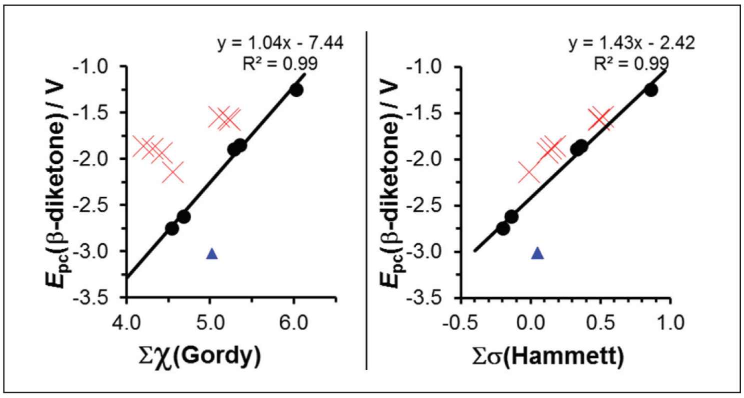


FIGURE 4: Illustration of the influence of R groups on the reduction potential (E_{pc} in V *vs* FcH/FcH$^+$) of β-diketones **1** – **15** in terms of the sum of the Gordy scale group electronegativities ($\chi_{R1} + \chi_{R2}$) (left) and the sum of Hammett meta substituent constants ($\sigma_{R1} + \sigma_{R2}$) (right). Data points of β-diketones with groups exhibiting pure inductive effect are shown with black circles (•), β-diketones having aromatic groups with red crosses (x) and the β-diketone with an ester group with a blue triangle (▲). The trend line is fitted through the black circles (pure inductive effect, compounds **2**, **5**, **6**, **10** and **12**). Data in Table 1.

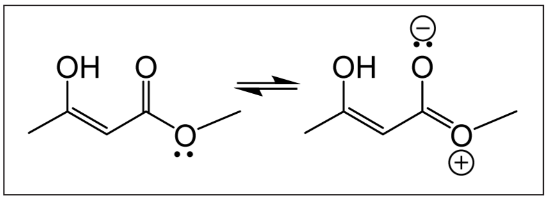


FIGURE 5: Electron donation via lone pair resonance in β-diketone **13**, resulting in more electron density on the β-diketone backbone.

linear relationship between E_{pc} and the calculated E_{LUMO} within the range as studied. A similar good relationship was obtained when using the hybrid B3LYP functional: $R^2 = 0.99$ for the gas phase calculations and 0.97 for calculations using CH_3CN as a solvent. Thus the energy of the LUMO, the orbital where the electron is added upon reduction, significantly influences the redox chemistry. The excellent interdependence of E_{pc} vs E_{LUMO} thus enables the prediction of the reduction potential of β-diketones, based on LUMO energies, with good accuracy.

The relationships obtained from DFT calculations taking the experimental solvent (CH_3CN) into account (instead of the gas phase), show a similar accuracy for the linear fit as obtained for the gas phase calculations. However, the slope of the reduction potential vs E_{LUMO} relationship is steeper for the solvent calculations, moving towards the ideal theoretical slope of -1, especially for the OLYP/TZP/CH_3CN calculations where the slope is -1.04(4) e^{-1}. The theoretical slope for reduction potential vs E_{LUMO} relationships is -1 due to the fact that LUMO energy relates directly to the absolute redox potential (Perdew and Levy 1997; Casida 1999; Hamel et al. 2002; Cardona et al. 2011). This implies that the product of E_{LUMO} with the electron charge (-1) gives absolute redox potential in eV. The y-axis intercept of the reduction potential *vs* E_{LUMO} graph, multiplied by the electron charge (-1), gives the absolute redox potential of the experimental reference system – namely of the ferrocene redox couple FcH/FcH$^+$. High-level *ab initio* molecular orbital theory benchmark calculated values for the absolute redox potentials of the ferrocene redox couple in acetonitrile are 4.988 V (when calculated at the G3(MP2)-RAD-Full-TZ level, using gas phase energies and COSMO-RS solvation energies) (Namazian et al. 2010) and +4.97 V (when calculated at the SMDB3LYP-D2/def2-QZVPPD//B3LYP/LanL2TZf/6-31G(d) level) (Romańczyk et al. 2014). Here we obtained 4.97(11) eV from OLYP/TZP/CH_3CN DFT calculations. Absolute redox potentials of β-diketones can thus be obtained from -E_{LUMO} (in eV) using OLYP/TZP/CH_3CN calculations. Results of similar accuracy are obtained by both functionals (B3LYP and OLYP) when relative energies are needed (similar R^2 values). However, when absolute redox potentials are required, the OLYP/TZP/CH_3CN DFT calculations gave the most accurate result.

TABLE 1: Reduction potential (E_{pc} in V *vs* FcH/FcH$^+$), group electronegativities (Gordy scale) and Hammett meta substituent σ constants of the indicated β-diketones $R^1COCHC(OH)R^2$.

	R^1	R^2	E_{pc} / V	$\chi R1$ [a]	$\chi R2$ [a]	$\chi R1 + \chi R2$	$\sigma R1$ [b]	$\sigma R2$ [b]	$\sigma R1 + \sigma R2$
1	CF_3	p-C_6H_4-NO_2	-1.045	3.01	–	–	0.43	–	–
2	CF_3	CF_3	-1.243	3.01	3.01	6.02	0.43	0.43	0.86
3	CF_3	Th	-1.541	3.01	2.10	5.11	0.43	0.09	0.52
4	C_6H_5	CF_3	-1.564	3.01	2.21	5.22	0.06	0.43	0.49
5	CF_3	CH_3	-1.851	3.01	2.34	5.35	0.43	-0.069	0.361
6	CF_3	$C(CH_3)_3$	-1.889	3.01	2.27	5.28	0.43	-0.10	0.33
7	Th	Th	-1.857	2.10	2.10	4.20	0.09	0.09	0.18
8	Th	Ph	-1.884	2.10	2.21	4.31	0.06	0.09	0.15
9	Ph	Ph	-1.934	2.21	2.21	4.42	0.06	0.06	0.12
10	CH_3	CH_3	-2.618	2.34	2.34	4.68	-0.069	-0.069	-0.138
11	C_6H_5	CH_3	-2.138	2.34	2.21	4.55	0.06	-0.069	-0.009
12	$C(CH_3)_3$	$C(CH_3)_3$	-2.748	2.27	2.27	4.54	-0.10	-0.10	-0.20
13	CH_3	OCH_3	-3.017	2.34	2.68	5.02	-0.069	0.12	0.051
14	CF_3	C_4H_2S-C_4H_3S	-1.470	3.01	–	–	0.43	–	–
15	CF_3	Fu	-1.581	3.01	2.230	5.240	0.43	0.06	0.49

a) The group electronegativity from references: du Plessis et al. 1998, Kagarise 1955, Conradie et al. 2008, Klaas 2002, Conradie and Conradie 2015.
b) The Hammett meta substituent σ constants from references: Hammett 1935, Hammett 1937, Hansch et al. 1991.

During the reduction process, the electron is added to the LUMO of the β-diketone. The LUMO of selected β-diketones are shown in Figure 7, where the locus of the added electron is visualised by the spin density plot of the reduced β-diketone. The shape of the spin density plot of a specific β-diketone-anion is similar to the shape of the LUMO of the neutral β-diketone. Evaluation of the spin density plots shows the effect of inductive and aromatic groups on the locus of the unpaired electron. Figure 7 indicates that the unpaired electron density of the reduced β-diketone is distributed over the aromatic core of the β-diketonate anion and extended over aromatic R groups if present. The electron density on the *pseudo*-aromatic backbone of the β-diketone decreases as more R groups become aromatic. β-diketones **2**$^{-}$, **5**$^{-}$, **6**$^{-}$, **10**$^{-}$ and **12**$^{-}$ containing two aliphatic groups, have on average around 90% spin density on the β-diketone backbone (C(OH)CHCO). However, β-diketones **1**$^{-}$, **2**$^{-}$, **4**$^{-}$, **11**$^{-}$, **14**$^{-}$ and **15**$^{-}$ with one aromatic and one aliphatic group have on average ca. 55% spin density on the β-diketone backbone (COCHC(OH)) and 30–60% on the aromatic group. β-diketones **7**$^{-}$, **8**$^{-}$, **9**$^{-}$ and **15**$^{-}$ with two aromatic groups have on average just over 50% spin density on the β-diketone backbone (COCHC(OH)) and 15–30% on each aromatic group. The large amount of 61% spin density is on the p-$C_6H_4NO_2$ group of **1**$^{-}$, resulting from a combination of the effect of an electron-withdrawing group (NO_2) and an aromatic group (phenyl).

The Molecular Electrostatic Potential (MESP) surface of selected molecules is illustrated in Figure 8. The electrostatic potential V(r) values present the positive and negative charged electrostatic potential in the molecule. The MESP surface in the outer regions of a molecule indicates how the latter is 'seen' by an approaching reactant. The sign of electrostatic potential in a surface region is determined by the predominance of negative charges contribution or positive charges contribution. Accordingly, the blue colour represents the positive region and it is prone to nucleophilic attack, the red colour shows the negative region which favours electrophilic attack, while green is neutral. The MESP surface of the neutral β-diketones is green to light blue, indicating that it is slightly prone to nucleophilic attack, i.e. it can be reduced. On the other hand, the MESP surface of the reduced β-diketones is yellow to red,

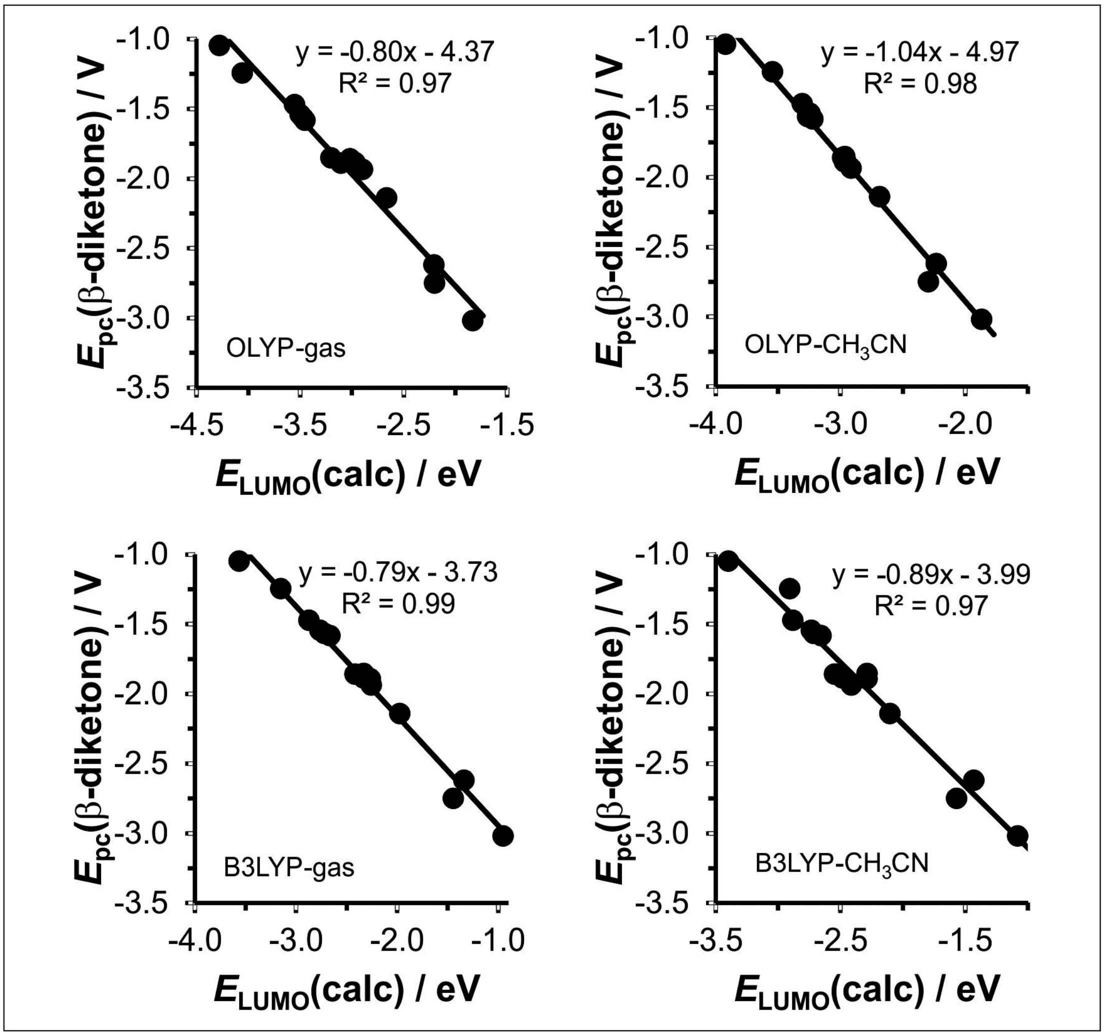


FIGURE 6: The relationships found between the experimental reduction potential (E_{pc} in V *vs* FcH/FcH^{+}) of β-diketones **1 – 15**, and the DFT calculated LUMO energy. Data in Supporting information Table S1.

illustrating the excess negative charge on the β-diketones. The negative region of β-diketone $\mathbf{10}^-$, with two aliphatic groups is concentrated over the β-diketone backbone (COCHC(OH)), while the negative region of β-diketone $\mathbf{11}^-$, with one aromatic and one aliphatic group is concentrated over both the β-diketone backbone and the aromatic group. The negative region of β-diketone $\mathbf{9}^-$, with two aromatic groups, is distributed throughout the molecule. A general trend is observed that the electrostatic potential on the enol-O atom decreases (less negative) as the experimental reduction potential of the β-diketone becomes less negative, see Figure 9. β-diketone **1** with the most positive reduction potential, also has the smallest electrostatic potential of enol-O atom, $V_{O\text{-enol}}$. A similar trend is observed for the electrostatic potential of the carbonyl-O atom.

Conclusion

The reduction potential of β-diketones, $R^1COCHC(OH)R^2$, containing aliphatic R groups with a principal σ inductive effect (R = CH_3, $C(CH_3)_3$ or CF_3), relates linearly to the accumulating electron-donating (or electron-withdrawing) effect of the R groups when expressed in terms of Hammett constants ($\sigma_{R1} + \sigma_{R2}$) or group electronegativities ($\chi_{R1} + \chi_{R2}$) of the R groups involved. However, the effect of an aromatic R group on the reduction potential of β-diketones is an interplay of the inductive effect through the σ-system and a resonance effect through the π-system, leading to a less negative reduction potential than expected (compound is more easily reduced) if only inductive effects are present. On the other hand, electron donation via lone pair resonance (on O of ester group R = OCH_3) leads to a more negative reduction potential than expected from a pure inductive effect due to increasing electron density on the backbone of the β-diketone. The DFT calculated energy of the LUMO of the β-diketones reflects the combined inductive and resonance effect of the R side groups of β-diketones. This is established from the linear relationship obtained between reduction potential E_{pc} of the β-diketones and density functional theory (DFT) calculated energies of the lowest unoccupied molecular orbital (E_{LUMO}) with R^2 = 0.97 - 0.99, depending on the DFT method used.

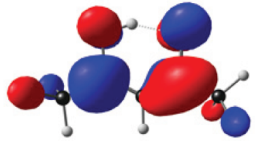
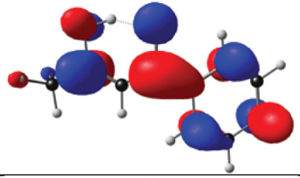
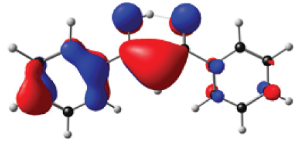
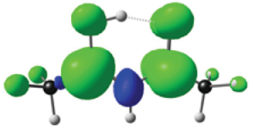
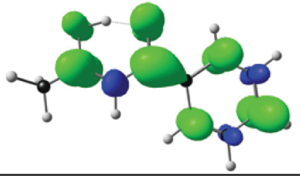
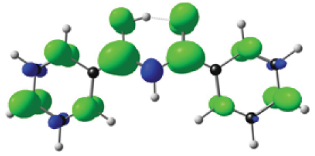
	10: no aromatic group	**11**: one aromatic group	**9**: two aromatic groups
LUMO neutral β-diketone			
spin plot reduced β-diketone			
% spin distribution R^1:(C(OH)CHCO):R^2	3:93:4	1:59:40	27:55:18

FIGURE 7: B3LYP/6-311G(d,p) LUMOs of the neutral β-diketones **9** – **11** and spin density plots of the reduced β-diketones $\mathbf{9}^-$ – $\mathbf{11}^-$. OLYP/TZP LUMOs/spin plots (not shown) are similar in shape. A contour of 0.05 and 0.005 e/Å3 was used for the MO and spin plots respectively.

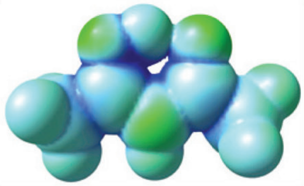
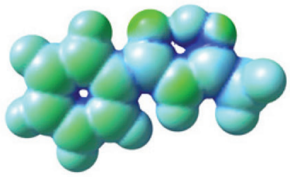
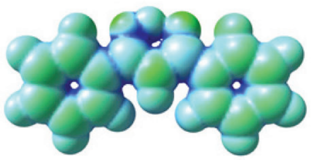
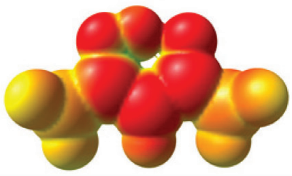
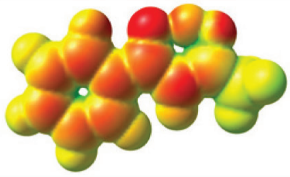
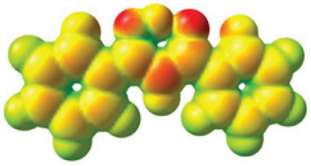
Neutral β-diketone			
Reduced β-diketone			
-0.15  0.15	**10**: no aromatic group	**11**: one aromatic group	**9**: two aromatic groups

FIGURE 8: Molecular electrostatic potential (MESP) of the indicated neutral and reduced β-diketones.

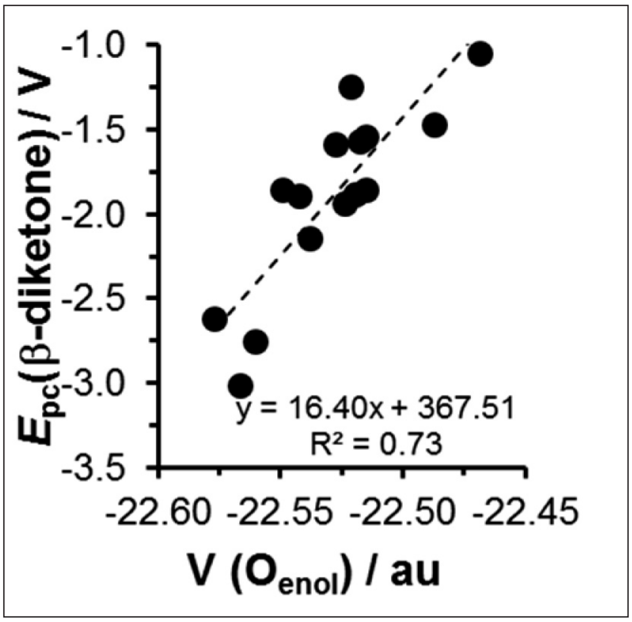


FIGURE 9: The correlation between the experimental reduction potential (E_{pc} in V *vs* FcH/FcH$^+$) and the MESP atomic potential of the enol-O atoms of reduced β-diketones **1**$^-$ – **15**$^-$.

Author contributions

JC and MMC conceptualised the project. NGSM did the experimental and computational work under supervision of JC and MMC. NGSM was responsible for the draft publication with revision and editing by JC and MMC.

Supporting information

Table S1 – S3 and optimised coordinates of the DFT calculations are provided in the Supporting Information.

Acknowledgements

This work has received support from the South African National Research Foundation (Grant numbers 113327, 96111 (JC) and 108960 (MMC)) and the Central Research Fund of the University of the Free State, Bloemfontein, South Africa. The High Performance Computing facility of the UFS is acknowledged for computer time.

References

Buchta, R.C., Evans, D.H., 1968. Electrochemical reduction of beta-diketones in dimethylsulfoxide. Analytical Chemistry 40, 2181-2186.

Buchta, R.C., Evans, D.H., 1970. Mechanism of the electrochemical reduction of enolized 1,3-diketones, Journal of the Electrochemical Society: Electrochemical Science 117, 1494-1500.

Cardona, C.M., Li, W., Kaifer, A.E., Stockdale, D., Bazan, G.C., 2011. Electrochemical considerations for determining absolute frontier orbital energy levels of conjugated polymers for solar cell applications. Advanced Materials 23, 2367-2371.

Casida, M.E., 1999. Correlated optimized effective-potential treatment of the derivative discontinuity and of the highest occupied Kohn-Sham eigenvalue: A Janak-type theorem for the optimized effective-potential model. Physical Review B: Condensed Matter 59, 4694-4698.

Conradie, M.M., Conradie, J., 2015. Electrochemical behaviour of Tris(β-diketonato) iron(III) complexes: A DFT and experimental study. Electrochimica Acta 152, 512-519.

Conradie, M.M., Muller, A.J., Conradie, J., 2008. Thienyl-containing β-diketones: Synthesis, characterisation, crystal structure and keto-enol kinetics. South African Journal of Chemistry 61, 13-21.

du Plessis, W.C., Vosloo, T.G., Swarts, J.C., 1998. β-Diketones containing a ferrocenyl group: synthesis, structural aspects, pKa' values, group electronegativities and complexation with rhodium(I). Dalton Transactions 15, 2507-2514.

Evans, D.H., O'Connell, K.M., Petersen, R.A., Kelly, M.J., 1983. Cyclic voltammetry. Journal of Chemical Education 60, 290-293.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A.V., Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F., Sonnenberg, J.L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., Fox, D.J., Gaussian, Inc., Wallingford CT, 2016. Gaussian 16, Revision B.01.

Gadre, S.R., Shirsat, R.N., 2000. Electrostatics of Atoms and Molecules. Universities Press, India.

Gritzner, G., Kuta, J., 1984. Recommendations on reporting electrode potentials in nonaqueous solvents. Pure and Applied Chemistry 56, 461-466.

Gschneidner Jr., K.A., Bünzli, J.-C.G., Pecharsky, V.K. 2005. Handbook on the Physics and Chemistry of Rare Earths, Volume 35, Elsevier.

Hamel, S., Duffy, P., Casida, M.E., Salahub, D.R., 2002. Kohn–Sham orbitals and orbital energies: fictitious constructs but good approximations all the same. Journal of Electron Spectroscopy Related Phenomena 123, 345-363.

Hammett, L.P., 1935. Some relations between reaction rates and equilibrium constants. Chemical Reviews 17, 125-136.

Hammett, L.P., 1937. The effect of structure upon the reactions of organic compounds. Benzene derivatives. Journal of the American Chemical Society 59, 96-103.

Hansch, C., Leo, A., Taft, R.W., 1991. A survey of Hammett substituent constants and resonance and field parameters. Chemical Reviews 91, 165-195.

Kagarise, R.E., 1955. Relation between the electronegativities of adjacent substitutents and the stretching frequency of the carbonyl group. Journal of the American Chemical Society
77, 1377-1379.

Katritzky, A.R., Wang, Z., Wang, M., Wilkerson, C.R., Hall, C.D., Akhmedov, N.G., 2004. Preparation of β-Keto esters and β-Diketones by C-acylation/ deacetylation of acetoacetic esters and acetonyl ketones with 1-Acylbenzotriazoles. Journal of Organic Chemistry 69, 6617-6622.

Klaas, P., 2002. Synthesis, electrochemical, kinetic and thermodynamic properties of new ferrocene-containing beta-diketonato rhodium(I) complexes with biomedical applications, M.Sc. Thesis, University of the Free State.

Klamt, A., 1995. Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena. Journal of Physical Chemistry 99, 2224-2235.

Klamt, A., Jones, V., 1996. Treatment of the outlying charge in continuum solvation models. Journal of Chemical Physics 105, 9972-9981.

Klamt, A., Schüürmann, G., 1993. COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. Journal of the Chemical Society, Perkin Transactions 2 5, 799-805.

Kuhn, A., von Eschwege, K.G., Conradie, J., 2011. Electrochemical and DFT-modeled reduction of Enolized 1,3-Diketones. Electrochimica Acta 56, 6211-6218.

Marenich, A.V., Cramer, C.J., Truhlar, D.G., 2009. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. Journal of Physical Chemistry B 113, 6378-6396.

McDaniel, D.H., Brown, H.C., 1958. An extended table of Hammett substituent constants based on the ionization of substituted benzoic acids. Journal of Organic Chemistry 23, 420-427.

Namazian, M., Lin, C.Y., Coote, M.L., 2010. Benchmark calculations of absolute reduction potential of Ferricinium/Ferrocene couple in nonaqueous solutions. Journal of Chemical Theory and Computation 6, 2721-2725.

Neal, T.E. Murray, R.W., 1970. Autocatalysis of the kinetic wave of acetylacetone in acetonitrile solvent. Analytical Chemistry 42, 1654-1656.

Perdew, J.P., Levy, M., 1997. Significance of the highest occupied Kohn-Sham eigenvalue. Physical Review B: Condensed Matter 56, 16021-16028.

Pombeiro, A.J.L., 2005. Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters. Journal of Organometallic Chemistry 690, 6021-6040.

Romańczyk, P.P., Rotko, G., Kurek, S.S., 2014. The redox potential of the phenyl radical/anion couple and the effect there on of the lithium cation: A computational study. Electrochemistry Communications 48, 21–23.

Sawyer, D.T., Roberts Jr., J.L., 1974. Experimental electrochemistry for chemists. John Wiley & Sons, New York.

Skyner, R.E., McDonagh, J.L., Groom, C.R., van Mourik, T., Mitchell, J.B.O., 2015. A review of methods for the calculation of solution free energies and the modelling of systems in solution. Physical Chemistry Chemical Physics 17, 6174-6191.

Stary, J., 1964. The solvent extraction of metal chelates, first ed. MacMillan, New York.

Te Velde, G., Bickelhaupt, F.M., Baerends, E.J., Fonseca Guerra, C., van Gisbergen, S.J.A., Snijders, J.G., Ziegler, T., 2001. Chemistry with ADF, Journal of Computational Chemistry 22, 931-967.

Vigato, P.A., Peruzzo, V., Tamburini,S., 2009. The evolution of β-diketone or β-diketophenol ligands and related complexes. Coordination Chemistry Reviews 253, 1099-1201.

Wells, P.R., 1968. Progress in Physical Organic Chemistry, John Wiley & Son Inc., New York, pp. 111-145.

Reduction potential of β-diketones: effect of electron donating, aromatic and ester substituent groups

Supporting information

Optimised Cartesian coordinates (Å)

All compounds were optimised with the OLYP functional in gas phase, using the triple-ζ basis set TZP.

TABLE OF CONTENTS

1. $CF_3C(OH)CHCO(PhNO_2)$

C	-0.866198000	0.501604000	-0.021758000
C	-1.854584000	1.503537000	0.016472000
C	-1.282603000	-0.843276000	-0.049350000
H	-1.547779000	2.544696000	0.035618000
H	-0.563680000	-1.654763000	-0.086693000
C	-3.208406000	1.180683000	0.031148000
C	-2.633777000	-1.180564000	-0.037521000
H	-3.970897000	1.952127000	0.062121000
H	-2.953671000	-2.216988000	-0.060767000
C	-3.584825000	-0.162780000	0.004705000
C	0.585305000	0.916036000	-0.031371000
C	1.639123000	-0.081473000	0.002847000
C	2.950208000	0.319849000	-0.002490000
C	4.128030000	-0.671735000	0.034248000
F	3.705100000	-1.967637000	0.062385000
F	4.919247000	-0.516226000	-1.063894000
F	4.896104000	-0.461328000	1.139838000
N	-5.039453000	-0.522608000	0.021921000
O	-5.855797000	0.406405000	0.050080000
O	-5.328449000	-1.725832000	0.008485000
O	3.340961000	1.583438000	-0.038266000
O	0.877802000	2.143923000	-0.061181000
H	2.447087000	2.092818000	-0.055891000
H	1.424324000	-1.138792000	0.038370000

2. $CF_3COCHC(OH)(PhNO_2)$

C	-0.853400000	0.448780000	0.075133000
C	-1.810092000	1.450834000	-0.177135000
C	-1.297289000	-0.871689000	0.280013000

H	-1.484976000	2.473425000	-0.337787000
H	-0.591618000	-1.665406000	0.506159000
C	-3.166222000	1.147690000	-0.232090000
C	-2.652701000	-1.183586000	0.235900000
H	-3.904351000	1.917080000	-0.431388000
H	-3.000713000	-2.196624000	0.407229000
C	-3.574458000	-0.168418000	-0.021097000
C	0.581929000	0.819794000	0.136259000
C	1.637691000	-0.065488000	-0.051007000
C	2.981870000	0.412866000	0.015839000
C	4.152016000	-0.623094000	-0.168232000
F	4.531373000	-1.107897000	1.054418000
F	3.781274000	-1.695155000	-0.935703000
F	5.231110000	-0.051860000	-0.749714000
N	-5.034435000	-0.496262000	-0.061330000
O	-5.820706000	0.434341000	-0.278032000
O	-5.358282000	-1.675662000	0.127733000
O	3.301744000	1.603069000	0.238493000
O	0.810469000	2.110818000	0.366922000
H	1.448561000	-1.104532000	-0.282393000
H	1.826395000	2.198363000	0.361577000

3. $CF_3COCHC(OH)CF_3$

C	1.193361000	0.414518000	-0.000034000
C	-0.010841000	-0.241545000	-0.000182000
C	-1.230815000	0.528939000	0.000023000
O	1.329412000	1.732925000	0.000307000
O	-1.271621000	1.771349000	0.000425000
H	-0.039117000	-1.323737000	-0.000560000
C	2.552205000	-0.316572000	-0.000169000
F	3.275043000	0.026994000	-1.101820000
F	3.274018000	0.024811000	1.102893000
F	2.399413000	-1.667017000	-0.001554000
H	0.382830000	2.083780000	0.000381000
C	-2.584443000	-0.282172000	-0.000128000
F	-3.659530000	0.528815000	-0.001261000
F	-2.651724000	-1.090197000	-1.103334000
F	-2.652828000	-1.088567000	1.104210000

4. $CF_3C(OH)CHCO(Th)$

C	2.251347000	-1.428725000	-0.000367000
C	1.929101000	-0.076157000	-0.000539000
S	3.379086000	0.893001000	0.000968000
C	4.373288000	-0.503628000	0.000683000
C	3.641680000	-1.672140000	0.000290000
H	1.515578000	-2.226048000	-0.000840000
H	5.453212000	-0.398879000	0.001163000
H	4.090270000	-2.662298000	0.000368000
C	0.615741000	0.585107000	-0.001282000
C	-0.587788000	-0.232350000	-0.000767000
C	-1.811212000	0.377189000	-0.000044000
C	-3.131317000	-0.411436000	0.000507000
F	-3.876606000	-0.109491000	-1.101398000
F	-2.923446000	-1.759586000	0.000551000
F	-3.875793000	-0.109296000	1.102893000
O	-1.988998000	1.691719000	0.000179000
O	0.533666000	1.849311000	-0.000090000
H	-0.535134000	-1.311426000	-0.000745000
H	-1.020411000	2.044544000	-0.000618000

5. $CF_3COCHC(OH)(Th)$

C	2.280084000	-1.462000000	-0.000095000
C	1.923414000	-0.118972000	-0.000011000
S	3.347384000	0.891012000	0.000154000
C	4.377518000	-0.477965000	0.000144000
C	3.675803000	-1.664818000	-0.000014000
H	1.561225000	-2.274833000	-0.000225000
H	5.453195000	-0.339734000	0.000240000
H	4.151416000	-2.641708000	-0.000067000
C	0.603060000	0.486079000	-0.000057000
C	-0.589898000	-0.241353000	-0.000072000
C	-1.828894000	0.448920000	0.000034000
C	-3.159219000	-0.384977000	0.000084000
F	-3.904827000	-0.093581000	-1.102670000
F	-2.944240000	-1.738397000	0.000049000
F	-3.904719000	-0.093622000	1.102921000
O	-1.953478000	1.700331000	0.000207000
O	0.584722000	1.819324000	-0.000131000
H	-0.569447000	-1.321719000	-0.000087000
H	-0.410119000	2.059818000	-0.000393000

6. $CF_3C(OH)CHCO(Ph)$

C	0.584791000	0.739664000	-0.000005000
C	-0.567355000	-0.145396000	0.001689000
C	-1.827125000	0.391009000	-0.000269000
C	-3.097113000	-0.477237000	0.001308000
F	-3.857378000	-0.224435000	-1.102467000
F	-2.805953000	-1.810140000	0.005463000
F	-3.859350000	-0.218064000	1.102226000
O	-2.080128000	1.689729000	-0.003863000
O	0.408499000	1.993501000	-0.003480000
H	-0.462886000	-1.219394000	0.004697000
H	-1.123359000	2.092395000	-0.004078000
C	1.977257000	0.181955000	0.000050000
C	3.066220000	1.074477000	0.002326000
C	2.248224000	-1.200664000	-0.002463000
C	4.376419000	0.601085000	0.002510000
C	3.560327000	-1.672123000	-0.002594000
C	4.629172000	-0.773969000	0.000047000
H	2.868853000	2.142363000	0.004153000
H	1.444693000	-1.929858000	-0.004871000
H	5.206806000	1.304891000	0.004516000
H	3.747634000	-2.744592000	-0.004802000
H	5.653295000	-1.144220000	0.000071000

7. $CF_3COCHC(OH)(Ph)$

C	0.580909000	0.656904000	-0.095996000
C	-0.561082000	-0.134374000	0.022672000
C	-1.848272000	0.466400000	-0.031356000
C	-3.116003000	-0.452100000	0.099128000
F	-3.928548000	-0.297313000	-0.982562000

F	-2.805093000	-1.783530000	0.189822000
F	-3.830057000	-0.126137000	1.213962000
O	-2.062016000	1.695511000	-0.173991000
O	0.467105000	1.974690000	-0.252151000
H	-0.474735000	-1.199565000	0.176599000
C	1.967540000	0.145709000	-0.048122000
C	3.034076000	1.052099000	0.110887000
C	2.263362000	-1.227307000	-0.161631000
C	4.349325000	0.597883000	0.166303000
C	3.580631000	-1.675452000	-0.110207000
C	4.628638000	-0.766187000	0.057616000
H	2.823674000	2.113033000	0.198276000
H	1.470675000	-1.954086000	-0.310723000
H	5.160127000	1.312210000	0.294938000
H	3.791373000	-2.738715000	-0.206738000
H	5.657370000	-1.119575000	0.099300000
H	-0.537992000	2.150213000	-0.248566000

8. CF$_3$C(OH)CHCO(CH$_3$)

C	2.178784000	-0.047440000	-0.000140000
C	0.835889000	-0.591129000	0.000126000
C	-0.229644000	0.273065000	0.000616000
C	-1.696025000	-0.194841000	-0.000126000
F	-2.349268000	0.272239000	-1.102474000
F	-1.798318000	-1.554122000	-0.000869000
F	-2.350129000	0.271095000	1.102197000
O	-0.101281000	1.587548000	0.001203000
O	2.369681000	1.200229000	0.000660000
H	0.672279000	-1.661343000	-0.000546000
C	3.365802000	-0.987948000	-0.000801000
H	3.070017000	-2.040002000	-0.007054000
H	3.990473000	-0.784574000	-0.878199000
H	3.983781000	-0.793793000	0.883536000
H	0.934585000	1.707426000	0.001829000

9. CF$_3$COCHC(OH)(CH$_3$)

C	2.147098000	-0.113628000	0.004441000
C	0.835549000	-0.557345000	0.031414000
C	-0.239632000	0.382535000	0.033709000
C	-1.709405000	-0.179641000	0.007583000
F	-2.161228000	-0.227327000	-1.284482000
F	-1.791013000	-1.450454000	0.513136000
F	-2.554520000	0.602257000	0.720794000
O	-0.097880000	1.624918000	0.019066000
O	2.447345000	1.182808000	-0.013434000
H	0.635797000	-1.621495000	0.050818000
C	3.334922000	-1.022801000	-0.005340000
H	3.038191000	-2.072800000	0.004576000
H	3.943701000	-0.826292000	-0.896054000
H	3.966112000	-0.816405000	0.867386000
H	1.552448000	1.656223000	-0.004354000

10. CF$_3$C(OH)CHCO(CMe$_3$)

C	1.213814000	0.506550000	0.000308000
C	-0.034897000	-0.244864000	0.000419000
C	-1.230390000	0.419033000	0.000073000
C	-2.588810000	-0.305284000	-0.000226000
F	-3.317853000	0.032978000	-1.102694000
F	-2.447035000	-1.661224000	0.000174000
F	-3.318705000	0.033558000	1.101490000
O	-1.349142000	1.740693000	-0.000139000
O	1.184120000	1.763417000	-0.000432000
H	-0.036979000	-1.325590000	0.000616000
C	2.562799000	-0.261451000	0.000153000
H	-0.367879000	2.047593000	-0.000111000
C	2.641828000	-1.154137000	-1.266027000
H	1.846791000	-1.904201000	-1.302918000
H	2.586717000	-0.554519000	-2.180543000
H	3.598307000	-1.688762000	-1.274092000
C	2.642757000	-1.153194000	1.266937000
H	1.847850000	-1.903334000	1.304925000
H	3.599311000	-1.687689000	1.274762000
H	2.588185000	-0.552898000	2.181044000
C	3.744819000	0.724423000	-0.000647000
H	3.733376000	1.369375000	0.881948000
H	4.685747000	0.163871000	-0.000804000
H	3.732702000	1.368733000	-0.883699000

11. CF$_3$COCHC(OH)(CMe$_3$)

C	1.180686000	0.399806000	0.027611000
C	-0.048175000	-0.240055000	-0.035836000
C	-1.257163000	0.517029000	-0.036043000
C	-2.609738000	-0.289571000	-0.060630000
F	-3.620304000	0.431986000	-0.596376000
F	-2.500134000	-1.452545000	-0.777547000
F	-2.965789000	-0.635225000	1.217946000
O	-1.324364000	1.765864000	0.014508000
O	1.244590000	1.728448000	0.088645000
H	-0.097696000	-1.317643000	-0.087895000
C	2.543327000	-0.294624000	0.018156000
C	2.418625000	-1.830524000	0.018723000
H	1.899455000	-2.200040000	0.908658000
H	1.897584000	-2.203334000	-0.868474000
H	3.420001000	-2.272354000	0.016935000
C	3.332900000	0.151008000	1.277084000
H	2.817086000	-0.152647000	2.194266000
H	4.320681000	-0.321293000	1.273751000
H	3.470148000	1.234197000	1.304304000
C	3.297390000	0.154737000	-1.262732000
H	3.429377000	1.238910000	-1.291006000
H	4.286679000	-0.313882000	-1.287591000
H	2.756878000	-0.149340000	-2.165381000
H	0.279297000	2.041103000	0.075400000

12. ThCOCHC(OH)(Th)

C	1.214649000	-0.527843000	-0.000055000
C	-0.004986000	0.130891000	-0.000008000
C	-1.233605000	-0.611146000	0.000042000
O	1.274277000	-1.862907000	-0.000093000
O	-1.240541000	-1.884752000	0.000074000
H	-0.020896000	1.211122000	-0.000013000

H	0.277946000	-2.141071000	-0.000070000
C	-2.763671000	1.492042000	-0.000027000
C	-2.512420000	0.126742000	0.000036000
S	-4.010656000	-0.762860000	0.000101000
C	-4.933731000	0.683926000	0.000042000
C	-4.140688000	1.810085000	-0.000022000
H	-1.986719000	2.249524000	-0.000081000
H	-6.017258000	0.634577000	0.000065000
H	-4.533810000	2.823659000	-0.000066000
C	2.776379000	1.519560000	-0.000029000
C	2.500018000	0.159674000	-0.000082000
S	3.981243000	-0.760041000	-0.000197000
C	4.931509000	0.667627000	-0.000189000
C	4.158768000	1.807893000	-0.000086000
H	2.010828000	2.288671000	0.000051000
H	6.013020000	0.592454000	-0.000262000
H	4.571660000	2.812990000	-0.000059000

13. ThC(OH)CHCO(Ph)

S	-3.984530000	-0.663409000	0.041149000
O	-1.346412000	-1.907186000	-0.311546000
O	1.147231000	-2.071815000	-0.358716000
H	-0.356153000	-2.232504000	-0.365308000
C	-4.836791000	0.814893000	0.220940000
H	-5.917935000	0.806242000	0.301005000
C	-3.993757000	1.904079000	0.243473000
H	-4.338751000	2.928995000	0.348627000
C	-2.637300000	1.534982000	0.112344000
H	-1.825245000	2.254628000	0.102788000
C	-2.451367000	0.164509000	-0.006483000
C	-1.213095000	-0.591362000	-0.146492000
C	0.045826000	-0.005712000	-0.101683000
H	0.127274000	1.055898000	0.078904000
C	1.224821000	-0.809739000	-0.211750000
C	2.572826000	-0.154712000	-0.111096000
C	2.776327000	1.201890000	-0.424398000
H	1.957102000	1.811384000	-0.796017000
C	4.036193000	1.784719000	-0.291952000
H	4.175214000	2.834569000	-0.545140000
C	5.115991000	1.025032000	0.163518000
H	6.096885000	1.483593000	0.278205000
C	4.929599000	-0.326515000	0.466429000
H	5.768130000	-0.923871000	0.819681000
C	3.673633000	-0.913608000	0.320875000
H	3.525818000	-1.964148000	0.553846000

14. ThCOCHC(OH)(Ph)

S	-4.012086000	-0.663092000	0.063728000
O	-1.326725000	-1.937567000	-0.270470000
O	1.194530000	-2.062498000	-0.333293000
H	0.188807000	-2.284810000	-0.334116000
C	-4.836480000	0.835453000	0.219371000
H	-5.917816000	0.852972000	0.302142000
C	-3.974721000	1.909672000	0.222124000
H	-4.300073000	2.943204000	0.310176000
C	-2.625005000	1.509911000	0.097152000
H	-1.801679000	2.216397000	0.075379000
C	-2.464257000	0.134382000	0.000387000
C	-1.237956000	-0.676249000	-0.134188000
C	0.038708000	-0.014534000	-0.088770000
H	0.091253000	1.050778000	0.081731000
C	1.214798000	-0.735389000	-0.187054000
C	2.559258000	-0.120727000	-0.094938000
C	2.779981000	1.232894000	-0.410858000
H	1.965537000	1.847836000	-0.783841000
C	4.048004000	1.794279000	-0.281224000
H	4.202557000	2.841136000	-0.536563000
C	5.119740000	1.016447000	0.165448000
H	6.108974000	1.458083000	0.271372000
C	4.915183000	-0.331587000	0.467913000
H	5.745278000	-0.944934000	0.813091000
C	3.649638000	-0.898761000	0.332587000
H	3.490999000	-1.945834000	0.571718000

15. PhCOCHC(OH)(Ph)

C	-1.217484000	0.787922000	-0.283683000
C	0.003878000	0.149822000	-0.145851000
C	1.236345000	0.872817000	-0.293915000
O	-1.277519000	2.089555000	-0.567156000
O	1.239744000	2.117631000	-0.544509000
H	0.020167000	-0.886281000	0.159635000
H	-0.281775000	2.365375000	-0.610164000
C	2.537371000	0.144311000	-0.105705000
C	2.657860000	-1.240298000	-0.324171000
C	3.674429000	0.858700000	0.307791000
C	3.874660000	-1.891664000	-0.124547000
C	4.886239000	0.203667000	0.523111000
C	4.991103000	-1.173633000	0.309435000
H	1.807299000	-1.817494000	-0.676218000
H	3.590181000	1.929489000	0.470226000
H	3.951158000	-2.962088000	-0.308526000
H	5.753770000	0.767526000	0.861024000
H	5.937504000	-1.685045000	0.478088000
C	-2.519288000	0.107869000	-0.095029000
C	-2.663539000	-1.277112000	-0.298783000
C	-3.642818000	0.850721000	0.308428000
C	-3.890811000	-1.901155000	-0.088069000
C	-4.866690000	0.221074000	0.527228000
C	-4.995675000	-1.156128000	0.332457000
H	-1.821828000	-1.868588000	-0.648130000
H	-3.542291000	1.920524000	0.464348000
H	-3.987247000	-2.971692000	-0.259408000
H	-5.723121000	0.807752000	0.853633000
H	-5.952606000	-1.646543000	0.501693000

16. $CH_3COCHC(OH)(CH_3)$

C	-1.206646000	-0.073632000	0.000028000
C	0.010418000	-0.720432000	0.000101000
C	1.244362000	0.023353000	0.000136000
O	-1.285517000	1.257510000	0.000011000
O	1.254139000	1.285770000	0.000040000
H	0.033262000	-1.805777000	0.000093000

H	-0.302090000	1.553361000	0.000071000
C	2.547552000	-0.754712000	-0.000061000
H	2.599499000	-1.408316000	0.880029000
H	2.599786000	-1.407233000	-0.880946000
H	3.401778000	-0.075736000	0.000462000
C	-2.527492000	-0.779379000	-0.000065000
H	-3.107485000	-0.484113000	-0.882528000
H	-2.400934000	-1.863895000	0.000064000
H	-3.107715000	-0.483920000	0.882180000

17. PhCOCHC(OH)(CH$_3$)

C	0.471368000	0.482083000	-0.171978000
C	1.461597000	-0.538247000	0.052824000
C	2.808148000	-0.239679000	0.006682000
O	0.816335000	1.679212000	-0.409621000
O	3.239938000	0.991364000	-0.257389000
C	3.887057000	-1.250196000	0.248878000
H	3.469274000	-2.234308000	0.471645000
H	4.532342000	-1.326301000	-0.634523000
H	4.519236000	-0.929736000	1.085427000
C	-0.988616000	0.131957000	-0.095379000
C	-1.922545000	1.144456000	0.183654000
C	-1.460747000	-1.178478000	-0.293932000
C	-3.281273000	0.850871000	0.284798000
C	-2.822285000	-1.468216000	-0.207604000
C	-3.736962000	-0.456045000	0.090532000
H	-1.566136000	2.160033000	0.329894000
H	-0.772698000	-1.981302000	-0.543736000
H	-3.990162000	1.643985000	0.516267000
H	-3.169535000	-2.486379000	-0.375507000
H	-4.798835000	-0.684416000	0.168454000
H	2.363709000	1.524559000	-0.375003000
H	1.169347000	-1.550105000	0.302224000

18. PhC(OH)CHCO(CH$_3$)

C	0.735759000	0.113121000	0.298658000
C	1.853404000	-0.611468000	-0.098429000
C	3.167403000	-0.078206000	0.099195000
O	0.894946000	1.302557000	0.870650000
O	3.349931000	1.054867000	0.643324000
C	4.372532000	-0.877764000	-0.353319000
H	4.096963000	-1.843299000	-0.786269000
H	4.932462000	-0.299970000	-1.098012000
H	5.043514000	-1.043223000	0.497086000
C	-0.668232000	-0.337939000	0.142821000
C	-1.700233000	0.422974000	0.722334000
C	-1.015203000	-1.502486000	-0.569246000
C	-3.031049000	0.030850000	0.598602000
C	-2.347046000	-1.890594000	-0.692499000
C	-3.361506000	-1.126829000	-0.108525000
H	-1.446704000	1.323229000	1.272199000
H	-0.251051000	-2.110769000	-1.043690000
H	-3.813041000	0.633112000	1.057073000
H	-2.595932000	-2.791852000	-1.249785000
H	-4.401716000	-1.431840000	-0.207244000
H	1.936198000	1.422967000	0.887900000
H	1.743696000	-1.587630000	-0.551655000

19. (CCH$_3$)C(OH)CHCO(CCH$_3$)

C	-1.222054000	-0.403550000	-0.000289000
C	-0.005677000	0.255110000	-0.000307000
C	1.232679000	-0.473338000	-0.000374000
O	-1.265588000	-1.733573000	-0.000453000
O	1.234696000	-1.740389000	-0.000223000
H	0.004489000	1.332590000	-0.000211000
H	-0.264268000	-2.001750000	-0.000760000
C	2.602257000	0.267215000	-0.000096000
C	-2.593604000	0.279573000	0.000047000
C	2.475571000	1.804739000	-0.001133000
H	1.955669000	2.177369000	-0.889902000
H	1.955168000	2.178564000	0.886839000
H	3.475110000	2.253644000	-0.001133000
C	3.376592000	-0.169704000	1.267328000
H	4.368178000	0.297250000	1.277701000
H	2.851893000	0.140600000	2.178150000
H	3.503029000	-1.254343000	1.298836000
C	3.378201000	-0.171276000	-1.265956000
H	3.504451000	-1.255969000	-1.296116000
H	2.854792000	0.138134000	-2.177829000
H	4.369892000	0.295471000	-1.275518000
C	-3.361034000	-0.171389000	1.269823000
H	-2.832881000	0.139201000	2.177961000
H	-4.355576000	0.287349000	1.284143000
H	-3.481156000	-1.256748000	1.300281000
C	-2.484752000	1.817182000	0.000055000
H	-1.966726000	2.192619000	-0.888156000
H	-3.489505000	2.252130000	0.000230000
H	-1.966422000	2.192606000	0.888095000
C	-3.361700000	-0.171314000	-1.269345000
H	-3.481650000	-1.256687000	-1.299916000
H	-4.356332000	0.287250000	-1.282998000
H	-2.834147000	0.139528000	-2.177746000

20. (OCH$_3$)COCHC(OH)(CH$_3$)

C	1.678486000	-0.089265000	0.094631000
C	0.467052000	-0.721009000	0.024389000
C	-0.772626000	0.022301000	0.095791000
O	1.799136000	1.243723000	0.231110000
O	-0.857010000	1.256759000	0.225466000
H	0.424559000	-1.798194000	-0.087588000
H	0.858527000	1.582040000	0.264444000
O	-1.865201000	-0.796535000	0.003802000
C	-3.157195000	-0.146586000	0.069975000
H	-3.285225000	0.367794000	1.027246000
H	-3.273771000	0.571265000	-0.747320000
H	-3.885459000	-0.954421000	-0.026761000
C	2.988514000	-0.809716000	0.031822000
H	3.597202000	-0.410318000	-0.787800000
H	3.548973000	-0.649118000	0.960807000
H	2.843616000	-1.881321000	-0.116770000

21. $(OCH_3)C(OH)CHCO(CH_3)$

opt to $(OCH_3)COCHC(OH)(CH_3)$

22. $CF_3C(OH)CHCO(ThTh)$

C	-3.808534000	0.305172000	0.017179000
C	-2.535604000	-0.187034000	-0.020843000
C	-1.402919000	0.732115000	0.000664000
O	-4.110276000	1.598260000	0.070086000
O	-1.591945000	1.984186000	0.051656000
H	-2.390539000	-1.256583000	-0.061287000
C	4.651655000	1.187641000	-0.215843000
C	3.889315000	0.035033000	-0.098059000
S	4.943612000	-1.358033000	0.045404000
C	6.355874000	-0.382874000	-0.060475000
C	6.047011000	0.949532000	-0.194577000
H	4.216249000	2.176019000	-0.327069000
H	7.333318000	-0.850180000	-0.015940000
H	6.798948000	1.729006000	-0.278968000
C	0.351831000	-1.158975000	-0.122180000
C	-0.048138000	0.170352000	-0.036506000
S	1.350574000	1.216952000	0.019778000
C	2.450558000	-0.133003000	-0.086316000
C	1.741662000	-1.330377000	-0.150190000
H	-0.338919000	-1.993580000	-0.171800000
H	2.223792000	-2.300146000	-0.228454000
C	-5.047486000	-0.602583000	-0.000237000
F	-5.820569000	-0.391679000	1.103588000
F	-5.816477000	-0.354176000	-1.100290000
F	-4.713939000	-1.925873000	-0.022775000
H	-3.183850000	2.040110000	0.073521000

23. $CF_3COCHC(OH)(ThTh)$

C	-3.809973000	0.404301000	0.033185000
C	-2.539399000	-0.217578000	-0.024943000
C	-1.383417000	0.571767000	0.009266000
O	-4.001255000	1.646594000	0.109250000
O	-1.474558000	1.900038000	0.098040000
H	-2.463907000	-1.293457000	-0.088692000
H	-2.483453000	2.082481000	0.121437000
C	4.584307000	1.190928000	-0.270407000
C	3.886418000	0.005911000	-0.090297000
S	5.007253000	-1.311836000	0.173082000
C	6.366115000	-0.266401000	0.028178000
C	5.988610000	1.034686000	-0.203603000
H	4.094414000	2.140568000	-0.463695000
H	7.366849000	-0.671421000	0.125418000
H	6.697186000	1.848757000	-0.327476000
C	0.378565000	-1.283846000	-0.174857000
C	-0.040159000	0.036158000	-0.043420000
S	1.338768000	1.103289000	0.060018000
C	2.457612000	-0.220143000	-0.093141000
C	1.771620000	-1.428314000	-0.202301000
H	-0.303720000	-2.123236000	-0.260474000
H	2.272874000	-2.384270000	-0.318875000
C	-5.092651000	-0.497494000	0.002207000
F	-5.849758000	-0.289712000	1.116201000
F	-5.858217000	-0.206020000	-1.087727000
F	-4.805065000	-1.837156000	-0.050410000

24. $CF_3COCHC(OH)(Fu)$

C	2.290442000	-1.604508000	-0.000125000
C	1.934272000	-0.270757000	-0.002556000
O	3.072281000	0.511462000	-0.005417000
C	4.128103000	-0.347012000	-0.000453000
C	3.707087000	-1.650905000	0.000588000
H	1.618993000	-2.453462000	0.001873000
H	5.106522000	0.115883000	0.000079000
H	4.336049000	-2.532837000	0.002833000
C	0.657507000	0.412871000	-0.002302000
C	-0.561799000	-0.268033000	-0.001535000
C	-1.773412000	0.470384000	0.000684000
C	-3.135045000	-0.314034000	0.000483000
F	-3.868912000	0.003185000	-1.103035000
F	-2.971109000	-1.675253000	0.002048000
F	-3.869863000	0.005458000	1.102661000
O	-1.847329000	1.725018000	-0.001374000
O	0.712750000	1.742526000	0.002258000
H	-0.579604000	-1.349119000	-0.003163000
H	-0.263952000	2.030935000	0.006468000

25. $CF_3C(OH)CHCO(Fu)$

C	2.253292000	-1.561048000	-0.004641000
C	1.945070000	-0.214303000	0.000027000
O	3.115893000	0.520898000	0.004250000
C	4.137014000	-0.379432000	0.000676000
C	3.666581000	-1.665963000	-0.002618000
H	1.553605000	-2.386779000	-0.008711000
H	5.134745000	0.041258000	0.002702000
H	4.260067000	-2.572571000	-0.004852000
C	0.675486000	0.521197000	0.000732000
C	-0.554435000	-0.258058000	0.000648000
C	-1.755635000	0.392418000	0.001493000
C	-3.103233000	-0.348047000	0.002734000
F	-3.838113000	-0.019646000	-1.098549000
F	-2.943200000	-1.703099000	0.002382000
F	-3.835910000	-0.019899000	1.105608000
O	-1.885925000	1.713597000	0.001052000
O	0.649319000	1.784157000	-0.001073000
H	-0.534783000	-1.338937000	0.000905000
H	-0.907576000	2.033668000	-0.001857000

26. Table S 1. B3LYP/6-311G(d,p) energies of 1 – 15

No	R1 and R2	isomer	gas				CH_3CN			
			E (a.u.)	E_{rel} (eV)	E_{LUMO} (eV)	$E_{LUMO, Boltzmann}$ (eV)	E (a.u.)	E_{rel} (eV)	E_{LUMO} (eV)	$E_{LUMO, Boltzmann}$ (eV)
1	CF_3, $PhNO_2$	enol-CF_3	-1040.035539	0.02	-3.511	-3.565	-1040.045257	0.04	-3.343	-3.398
		enol-$PhNO_2$	-1040.036274	0.00	-3.590		-1040.046752	0.00	-3.409	
2	CF_3, CF_3	-	-941.496651	---	-3.153	-3.153	-941.501474	---	-2.907	-2.907
3	CF_3, Th	enol-CF_3	-1156.247904	0.00	-2.711	-2.765	-1156.254830	0.01	-2.668	-2.735
		enol-Th	-1156.247530	0.01	-2.844		-1156.255067	0.00	-2.787	
4	CF_3, Ph	enol-CF_3	-835.483274	0.03	-2.628	-2.721	-835.489262	0.05	-2.612	-2.715
		enol-Ph	-835.484281	0.00	-2.753		-835.490952	0.00	-2.732	
5	CF_3, CH_3	enol-CF_3	-643.701043	0.05	-2.238	-2.330	-643.706499	0.07	-2.142	-2.288
		enol-CH_3	-643.702966	0.00	-2.342		-643.708919	0.00	-2.299	
6	CF_3, CMe_3	enol-CF_3	-761.672692	0.04	-2.192	-2.267	-761.677508	0.05	-2.149	-2.289
		enol-CMe_3	-761.674320	0.00	-2.280		-761.679411	0.00	-2.308	
7	Th, Th	-	-1370.993056	---	-2.417	-2.417	-1371.002377	---	-2.548	-2.548
8	Th, Ph	enol-Th	-1050.228521	0.04	-2.360	-2.336	-1050.237007	0.05	-2.498	-2.485
		enol-Ph	-1050.230026	0.00	-2.331		-1050.238684	0.00	-2.483	
9	Ph, Ph	-	-729.465414	---	-2.256	-2.256	-729.473250	---	-2.414	-2.414
10	CH_3, CH_3	-	-345.903104	---	-1.339	-1.339	-345.908716	---	-1.432	-1.432
11	Ph, CH_3	enol-CH_3	-537.684845	0.00	-1.967	-1.975	-537.691531	0.00	-2.106	-2.106
		enol-Ph	-537.683698	0.03	-2.000		-537.690433	0.03	-2.104	
12	CMe_3, CMe_3	-	-581.844868	---	-1.446	-1.446	-581.849163	---	-1.571	-1.571
13	CH_3, OCH_3	enol-CH_3	-421.153170	0.00	-0.952	-0.952	-421.158573	0.00	-1.081	-1.081
		enol-OCH_3	-421.139090	0.38	-0.956		-421.145392	0.36	-1.108	
14	CF_3, ThTh	enol-CF_3	-1708.122729	0.00	-2.822	-2.874	-1708.131062	0.01	-2.821	-2.883
		enol-ThTh	-1708.122426	0.01	-2.945		-1708.131369	0.00	-2.927	
15	CF_3, Fu	enol-CF_3	-833.260664	0.01	-2.584	-2.667	-833.268992	0.02	-2.568	-2.657
		enol-Fu	-833.260910	0.00	-2.731		-833.269640	0.00	-2.702	

27. **Table S 2. OLYP/TZP energies of 1 – 15**

No	R1 and R2	isomer	gas				CH_3CN			
			E (eV.)	E_{rel} (eV)	E_{LUMO} (eV)	$E_{LUMO,\ Boltzmann}$ (eV)	E (eV)	E_{rel} (eV)	E_{LUMO} (eV)	$E_{LUMO,\ Boltzmann}$ (eV)
1	CF_3, $PhNO_2$	enol-CF_3	-150.04	0.05	-4.249	-4.280	-150.41	0.09	-3.921	-3.921
		enol-$PhNO_2$	-150.09	0.00	-4.284		-150.49	0.00	-3.921	
2	CF_3, CF_3	-	-86.20	---	-4.060	-4.060	-86.40	---	-3.546	-3.546
3	CF_3, Th	enol-CF_3	-114.34	0.02	-3.425	-3.501	-114.57	0.06	-3.175	-3.244
		enol-Th	-114.36	0.00	-3.530		-114.62	0.00	-3.252	
4	CF_3, Ph	enol-CF_3	-135.37	0.06	-3.405	-3.474	-135.55	0.09	-3.200	-3.265
		enol-Ph	-135.43	0.00	-3.481		-135.64	0.00	-3.267	
5	CF_3, CH_3	enol-CF_3	-85.61	0.07	-3.226	-3.202	-85.80	0.09	-2.971	-2.967
		enol-CH_3	-85.68	0.00	-3.201		-85.89	0.00	-2.967	
6	CF_3, CMe_3	enol-CF_3	-133.02	0.06	-3.066	-3.106	-133.17	0.08	-2.884	-2.968
		enol-CMe_3	-133.09	0.00	-3.110		-133.24	0.00	-2.972	
7	Th, Th	-	-142.33	---	-3.019	-3.019	-142.60	---	-2.983	-2.983
8	Th, Ph	enol-Th	-163.37	0.03	-2.995	-2.970	-163.65	0.00	-2.955	-2.957
		enol-Ph	-163.41	0.00	-2.964		-163.61	0.03	-2.966	
9	Ph, Ph	-	-184.45	---	-2.898	-2.898	-184.65	---	-2.917	-2.917
10	CH_3, CH_3	-	-84.98	---	-2.209	-2.209	-85.18	---	-2.234	-2.234
11	Ph, CH_3	enol-CH_3	-134.72	0.00	-2.664	-2.664	-134.92	0.00	-2.687	-2.688
		enol-Ph	-134.72	0.00	-2.664		-134.91	0.01	-2.690	
12	CMe_3, CMe_3	-	-179.75	---	-2.202	-2.202	-179.87	---	-2.297	-2.297
13	CH_3, OCH_3	enol-CH_3	-91.44	0.00	-1.834	-1.834	-91.63	0.00	-1.871	-1.871
		enol-OCH_3	-91.00	0.44	-1.993		-91.00	0.63	-2.025	
14	CF_3, ThTh	enol-CF_3	-159.05	0.05	-3.466	-3.554	-159.31	0.08	-3.239	-3.308
		enol-ThTh	-159.10	0.00	-3.569		-159.39	0.00	-3.311	
15	CF_3, Fu	enol-CF_3	-116.81	0.04	-3.367	-3.454	-117.09	0.05	-3.152	-3.221
		enol-Fu	-116.84	0.00	-3.473		-117.14	0.00	-3.230	

28. **Table S 3. MESP potential on O of B3LYP/6-311G(d,p) optimised geometries of reduced 1 – 15.**

				MESP Potential	
No	**R 1**	**R 2**	**isomer**	**O-enol**	O_{CO}
1	CF_3	Ph-NO_2	enol-CF_3	-22.468	-22.52
			enol-PhNO_2	-22.468	-22.52
2	CF_3	CF_3		-22.522	-22.58
3	CF_3	Th	enol-CF_3	-22.515	-22.58
			enol-Th	-22.512	-22.57
4	CF_3	Ph	enol-CF_3	-22.521	-22.58
			enol-Ph	-22.518	-22.57
5	CF_3	CH_3	enol-CF_3	-22.548	-22.61
			enol-CH_3	-22.549	-22.61
6	CF_3	tBu	enol-CF_3	-22.541	-22.60
			enol-tBu	-22.542	-22.60
7	Th	Th		-22.515	-22.57
8	Ph	Th	enol-Th	-22.519	-22.57
			enol-Ph	-22.520	-22.57
9	Ph	Ph		-22.524	-22.58
10	CH_3	CH_3		-22.577	-22.64
11	CH_3	Ph	enol-CH_3	-22.538	-22.60
			enol-Ph	-22.537	-22.59
12	CMe_3	CMe_3		-22.561	-22.62
13	OCH_3	CH_3	enol-CH_3	-22.567	-22.62
			enol-OCH_3	-22.566	-22.63
14	CF_3	ThTh	enol-CF_3	-22.487	-22.55
			enol-ThTh	-22.486	-22.54
15	CF_3	Fu	enol-CF_3	-22.529	-22.59
			enol-Fu	-22.527	-22.58