# NATURAL BOND ORBITAL ANALYSIS OF CYCLIC AND ACYCLIC "C-H" ACIDS

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**Keywords:** Meldrum's acid, barbituric acid, tetronic acid, carbon acidity donor-acceptor interactions, DFT calculations, NBO analysis.

The high acidity of Meldrum's acid, barbituric and tetronic acids in comparison to their acyclic analogues was explained by density functional theory and calculations and by natural bond orbital analysis. The present study shows that cyclic β-dicarbonyl compounds are remarkably stabilized by intramolecular donor-acceptor interactions and this effect is absent in their acyclic analogues.

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## Introduction

The high C-H acidity[1] of several precursors in multicomponent reactions[2] is the key for efficient acid-base synthesis. The increase of acidity in cyclic dicarbonyl compounds allows easy formation of carbon anions in Knoevenagel, Michael, or aldolisation reactions. This increase, due to the cyclic structure of compounds, was also employed in solventless reactions.[2] This phenomenon observed in experiment for various acids such as barbituric acid (BA), Meldrum's acid (MA), tetronic acid (TA) did not receive many explanations besides some few theoretical works on Meldrum's acid. The C- H acidity of these cyclic compounds in water (p$K_a$(MA) = 4.83, (p$K_a$ (BA) = 4.01) and (p$K_a$(TA) = 3.76)[4] are comparable to that of acetic acid (p$K_a$ =4.75). This relatively high acidity is due to the acid hydrogen bonded to carbon positioned between the two carbonyl groups. The C- H acidity of these cyclic β-dicarbonyl compounds is found to be remarkably higher than that of the related compounds with open chains, namely, diethyl malonate (DEM), malonamide (MNA) and ethyl acetoacetate (EAA) (Figure 1). The experimental p$K_a$ values for these acyclic compounds are p$K_a$ (DEM) = 13.3, p$K_a$ (MNA) = 12.5) and p$K_a$ (EAA) = 10.7.

Some experimental and theoretical works devoted to the spectacular high acidity of MA, BA and TA can be found in the literature.[4] Arnett and Harrelson[5] suggested that the high acidity of Meldrum's acid compared to dimethyl malonate, results from the restricted rotation around the ester bonds in the six-membered ring of MA. These authors also observed that the acidity decreased rapidly when going from the six-membered to the ten-membered ring. Interestingly, it has been found that the p$K_a$ of the thirteen-membered ring is closer to that of (acyclic) methyl malonate. Wang and Houk[6]

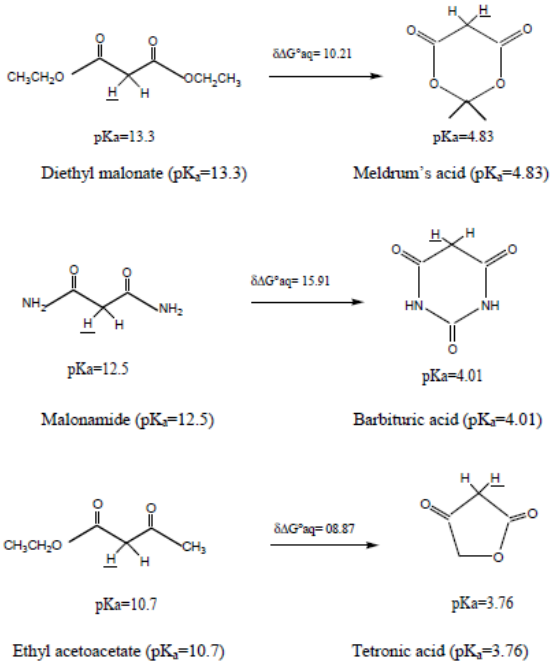



**Figure 1.** The relative values calculated δΔ$G$°aq of studied compounds.

suggested that the significant acidity of MA can be explained by differences in steric and electrostatic (dipole-dipole) repulsions between *E* and *Z* conformers of esters in the neutral and anionic species. Likewise, Wiberg and Laidig[7] showed, by theoretical calculations, that the surprising high acidity of MA, displaying an ester conformation with a bis(*E*) ester conformation, can be attributed to the difference in acidity between *Z* and *E* rotameres of methyl acetate. The solvent effects on acidities of *Z* and *E* ester conformers were also studied by Evanseck et al.[8] Their calculations showed an appreciable stabilization of the *E* conformer in comparison of the *Z* conformer by 3.0 22 kcal mol$^{-1}$ in water and 2.7 kcal mol$^{-1}$ in acetonitrile. Furthermore, the anionic form of the *E* conformer is also found to be more stable than that of the *E* conformer by 2.3 22 kcal mol$^{-1}$ in water and .1.5 kcal mol$^{-1}$ in acetonitrile. The difference in acidity observed in aqueous phase between MA and dimethyl malonate were also explained by conversion of two *Z* esters groups into two *E*

esters groups.[8-9] Gao et al.[9] showed that the solvent effects are rather weak and the major stabilization of the enolate anion is due to the stereoelectronic effects, called anomeric effects which represent an important factor for explaining the origin of the noteworthy acidity of the MA. Our aim in this work is to explain the origin of the remarkably high acidity of MA, BA and TA using the Natural Bond Orbital (NBO) analysis and the quantification of electron populations and intramolecular donor-acceptor interactions.[10-14]

## Computational procedures

All the calculations reported in this work were carried out using the Gaussian 03W computational package.[15] The geometries of the neutral and anionic (deprotonated) species are fully optimized at the B3LYP[16] level of theory in combination of the standard 6-311++G(d,p) basis set. Solvent effects are taken into account using SCRF (self-consistent reaction field) calculations using PCM (polarizable continuum model).[17-19] NBO analysis[10-14] was performed using the NBO 3.1 program[20] implemented in Gaussian 03W package.

### NBO analysis

Several methods have been used to analyze the contribution of localized orbitals in molecular properties.[10-11] In addition of stabilization effects, the stereoelectronic interactions also provide the manner of transmitting information between the various parts of the molecule. For example, the NBO method was employed to establish the electronic exchanges, the electronic transfer between donor-acceptor compounds and hyperconjugation interactions.[13,21-23]

In the NBO analysis, the donor–acceptor (bond–antibond) interactions are considered by examining all possible interactions between the 'occupied' (donor) Lewis-type NBOs and the 'non occupied' (acceptor) non-Lewis NBOs. Then, their energies are estimated by second-order perturbation theory. These stabilizing interactions are referred as 'delocalization' corrections to the 0th-order natural Lewis structure. For each donor, NBO (*i*) and acceptor NBO (*j*), the stabilization energy $E^{(2)}$, which is associated with the $i \rightarrow j$ delocalization, is explicitly estimated by the following equation:

$$E^{(2)}_{i\rightarrow j^*} = -n^{(0)}_i \frac{\langle \varphi^{(0)}_i / \hat{F} / \varphi^{(0)}_{j^*} \rangle^2}{\varepsilon^{(0)}_{j^*} - \varepsilon^{(0)}_i} \qquad (1)$$

where

$n_i$ is the orbital occupancy,

$\varepsilon_i$, $\varepsilon_j$ are NBO orbital energies and

$F$ is the Fock operator.

To further understanding of the electronic effects in cyclic and acyclic β-dicarbonyl compounds, NBO analysis, using B3LYP/6-311++G** geometries, has been carried out. Second order delocalization energies $E^{(2)}$, which are quantitative representation of the stabilization energies associated with the electronic delocalization, are discussed and analysed in the present work.

## Results and discussions

### Calculations of the free energies of deprotonation ΔG°

Energies of deprotonation at 298 K in gas,[24] $\Delta G°_{(gas)}$ and in aqueous phase, $\Delta G°_{(aq)}$, were calculated using the B3LYP/6-311++G(d, p) computational level. The results are given in table 1.

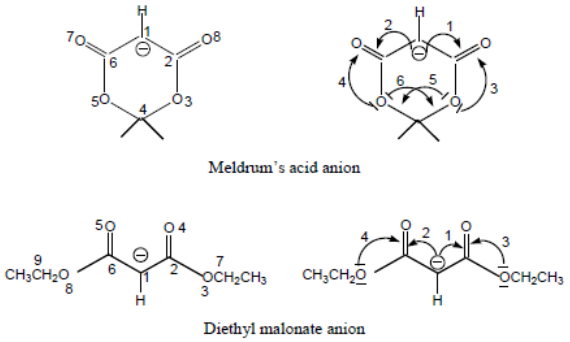
**Table 1.** B3LYP/6-311++G(d, p) energies of deprotonation (kcal mol$^{-1}$) in gas phase $\Delta G°_{gas}$ and in aqueous phase $\Delta G°_{aq}$ of the β-dicarbonyl compounds.

| Compound | $\Delta G°_{gas}$ | $\Delta G°_{aq}$ | p$K_a$(exp) |
|---|---|---|---|
| Diethyl malonate | 336.62 | 22.31 | 13.30 |
| Meldrum's acid | 321.34 | 12.10 | 4.83 |
| Malonamide | 340.31 | 27.22 | 12.50 |
| Barbituric acid | 316.57 | 11.31 | 4.01 |
| Ethyl acetylacetate | 331.50 | 19.31 | 10.70 |
| Tetronic acid | 319.21 | 10.44 | 3.76 |

The difference, $\delta\Delta G°_{aq}$, between cyclic acids and their acyclic analogues are given in Figure 1**.** It turns out that $\Delta G°_{aq}$ of all cyclic compounds are lower than those of their acyclic analogues. For instance, the free Gibbs enthalpy of MA is lower by 10.21 kcal mol$^{-1}$ than that of DEM, indicating the high acidity of cyclic compounds in comparison of open-chain compounds. In order to explain the difference in acidity between the cyclic β-dicarbonyl compounds and their open chain analogues, we have explored all the orbital interactions and the electronic effect of delocalization in the conjugate bases of these acids.

### Case 1: Meldrum's acid / diethyl malonate

The most significant stereoelectronic interactions in the conjugate bases (anions) of the MA and DEM are illustrated in Scheme 1. The stabilization energies, expressed in terms of $E^{(2)}$, are given in Table 2. The acyclic anions are asymmetrical and their geometry is in sickle form, so both C=O are not directed in the same direction.[25] In the cyclic anions, there is symmetry (form W) in the Meldrum anion and barbiturate.




**Scheme 1.** The most significant stereoelectronic interactions of MA and DEM anions.

The acidity of these dicarbonyl compounds (cyclic and acyclic) is attributed to the hydrogen positioned between the two carbonyl groups which facilitate the deprotonation process. NBO analysis shows that the negative charge on

carbon atom $C_1$ of MA and DEM anions are strongly delocalized on the two carbonyl groups (C=O) by charge transfer $n_{C1}\rightarrow\pi^*_{C=O.}$ As can be seen from the Table 2**,** there is a significant stabilization energy for $n_{C1}\rightarrow\pi^*_{C=O}$ delocalization in Meldrum' acid and DEM anions ($E^{(2)}$ =105 and 132 22 kcal mol$^{-1}$ respectively). The two compounds also exhibited a second donor-acceptor interactions of the type $n_O\rightarrow\pi^*_{C=O}$ between the lone pair of the ester oxygen and the unoccupied orbital π* of the carbonyl group. The $E^{(2)}$ stabilization energies are 22.68 22 kcal mol$^{-1}$ (twice) for MA and 29.70 and 36.22 kcal mol$^{-1}$ in diethylmalonate (see Table 2).

**Table 2.** $E^{(2)}$ energies of the main donor-acceptor interactions for MA and DEM anions.

| **Meldrum's (MA) anion** | |
|---|---|
| Interaction | E$^{(2)}$ (kcal mol$^{-1}$) |
| 1. $n_{C1}\rightarrow\pi^*_{C2=O8}$ | 105.06 |
| 2. $n_{C1}\rightarrow\pi^*_{C6=O7}$ | 105.06 |
| 3. $n_{O3\,(LP2)}\rightarrow\pi^*_{C2=O8}$ | 22.68 |
| 4. $n_{O5\,(LP2)}\rightarrow\pi^*_{C6=O7}$ | 22.68 |
| 5. $n_{O3\,(LP1)}\rightarrow\sigma^*_{C4-O5}$ | 4.00 |
| $n_{O3\,(LP2)}\rightarrow\sigma^*_{C4-O5}$ | 8.00 |
| 6. $n_{O5\,(LP1)}\rightarrow\sigma^*_{C4-O3}$ | 4.00 |
| $n_{O5\,(LP2)}\rightarrow\sigma^*_{C4-O3}$ | 8.00 |
| 7. $n_{O3\,(LP1)}\rightarrow\sigma^*_{C2-C1}$ | 3.77 |
| 8. $n_{O5\,(LP1)}\rightarrow\sigma^*_{C6-O1}$ | 3.77 |
| **Diethyl malonate (DEM) anion** | |
| Interaction | $E^{(2)}$ (kcal mol$^{-1}$) |
| 1. $n_{C1}\rightarrow\pi^*_{C2=O4}$ | 132.35 |
| 2. $n_{C1}\rightarrow\pi^*_{C6=O5}$ | 132.19 |
| 3. $n_{O3(LP2)}\rightarrow\pi^*_{C2=O4}$ | 29.70 |
| 4. $n_{O8(LP2)}\rightarrow\pi^*_{C6=O5}$ | 36.22 |

In Table 3, we have calculated by NBO analysis the electron occupations of the orbitals including the various interactions donor-acceptor for MA and DEM anions.

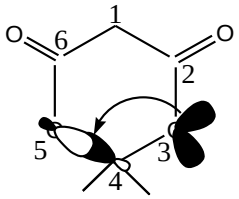
The analysis of these occupations, for the two compounds, shows that orbitals $\pi^*_{C=O}$ which are "usually" vacant, have an occupation of 0.40 - 0.44 electrons and the occupation of the negative charge of carbon $C_1$ is lower than 2 electrons (1.35 and 1.37 electrons for MA and DEM respectively). The second lone pair occupancies of ester oxygen atoms $n_O$ are also decreased (1.836 - 1.865 electrons) due to charge transfer interactions (See table 3). These results confirm the $E^{(2)}$ values previously found (Table 2 ) corresponding to $n_O\rightarrow\pi^*_{C=O}$ donor-acceptor interactions.

In addition to $n_C\rightarrow\pi^*_{C=O}$ and $n_O\rightarrow\pi^*_{C=O}$ interactions, MA presents other important interactions (which are absent in DEM). Indeed, for MA, there is a charge transfer of the type $n_O\rightarrow\sigma^*_{C-O}$ due to the donor-acceptor interaction between the nonbonding electron pairs of ester oxygens and antibonding orbitals of the vicinal sigma bonds. These interactions are called anomeric stabilization or anomeric effects (Scheme 2). These effects are very frequent in cyclic bilactone compounds like MA. The sum of $E^{(2)}$ energies of these interactions (orbitals of the four lone pairs of two ester oxygens and the two vicinal sigma antibonding orbitals $\sigma^*_{C4-O5}$ and $\sigma^*_{C4-O3}$) are of the magnitude 21.6 22 kcal mol$^{-1}$ (Table 2). Gao et al.[9] showed that the dissociation of the MA is accompanied by an increase of $E^{(2)}$ stabilization energy due to anomeric effects. The analysis of the occupancies of the antibonding orbitals indicated that anomeric effects lead to an occupancy of $\sigma^*_{C4-O5}$ and $\sigma^*_{C4-O3}$ orbitals by 0.10 electrons.

**Table 3.** Electron Occupancies of orbitals calculated by NBO method.

| **Compound** | **Orbital** | **Occupancy** |
|---|---|---|
| Meldrum's (MA) anion | $n_{C1}$ | 1.350 |
| | $\pi^*_{C2=O8}$ | 0.405 |
| | $\pi^*_{C6=O7}$ | 0.405 |
| | $n_{O3(LP2)}$ | 1.856 |
| | $n_{O5(LP2)}$ | 1.856 |
| | $\sigma^*_{C4-O5}$ | 0.100 |
| | $\sigma^*_{C4-O3}$ | 0.100 |
| Diethyl malonate (DEM) anion | $n_{C1}$ | 1.370 |
| | $\pi^*_{C2=O4}$ | 0.435 |
| | $\pi^*_{C5=O6}$ | 0.435 |
| | $n_{O3(LP2)}$ | 1.845 |
| | $n_{O8(LP2)}$ | 1.845 |

These anomeric effects present in the MA anion, which are completely absent in DEM anion, lead to a substantial stabilization of the MA conjugate base and therefore make an important contribution in increasing of the acidity of the cyclic MA compound in comparison with its corresponding acyclic compound (DEM).

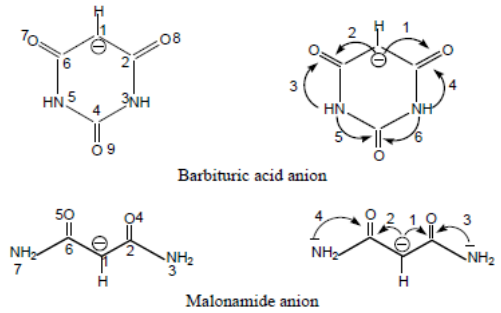



**Scheme 2.** Anomeric effects in MA.

**Case 2: Barbituric acid/malonamide**

The main interactions donor-acceptor and their corresponding stabilization $E^{(2)}$ energies for cyclic BA anion and its acyclic analogous compound, namely MNA anion are given in scheme 3 and Table 4, respectively.

NBO analysis shows that the negative charge on carbon atom $C_1$ of BA and MNA are strongly delocalized with the two carbonyl groups (C=O) via vicinal charge transfer interactions. For the BA anion, $E^{(2)}$ =79.07 kcal mol$^{-1}$ for $n_{C1}\rightarrow\pi^*_{C2=O8}$ and 78.28 kcal/mol for $n_{C1}\rightarrow\pi^*_{C6=O7}$). For MNA anion, $E^{(2)}$ = 100.84 kcal/mol for $n_{C1}\rightarrow\pi^*_{C2=O4}$ and 92.08 kcal mol$^{-1}$ for $n_{C1}\rightarrow\pi^*_{C6=O5}$ interactions. BA and MNA also exhibited a second type of donor-acceptor interactions involving the lone pair of the nitrogen atoms and the antibonding π* orbitals of the adjacent carbonyl groups. For BA anion, $E^{(2)}$ =49.60 kcal/mol for $n_{N5}\rightarrow\pi^*_{C6=O7}$ interaction and $E^{(2)}$=50.39 kcal/mol for $n_{N3}\rightarrow\pi^*_{C2=O8}$ interaction. For MNA anion, $E^{(2)}$ = 22.51 kcal/mol for $n_{N3}\rightarrow\pi^*_{C2=O4}$ and 18.84 kcal mol$^{-1}$ for $n_{N7}\rightarrow\pi^*_{C6=O5}$ interactions (Table 4).




**Scheme 3.** The important stereoelectronic interactions of BA and MNA anions.

**Table 4.** $E^{(2)}$ energies of the main donor-acceptor interactions for BA and MNA anions.

| Barbituric acid (BA) anion | | Malonamide (MNA) anion | |
|---|---|---|---|
| **Interaction** | **$E^{(2)}$ (kcal mol$^{-1}$)** | **Interaction** | **$E^{(2)}$ (kcal mol$^{-1}$)** |
| $n_{C1}\rightarrow\pi^*_{C2=O8}$ | 79.07 | $n_{C1}\rightarrow\pi^*_{C2=O4}$ | 100.84 |
| $n_{C1}\rightarrow\pi^*_{C6=O7}$ | 78.29 | $n_{C1}\rightarrow\pi^*_{C6=O5}$ | 92.08 |
| $n_{N5}\rightarrow\pi^*_{C6=O7}$ | 49.60 | $n_{N3}\rightarrow\pi^*_{C2=O4}$ | 22.51 |
| $n_{N3}\rightarrow\pi^*_{C2=O8}$ | 50.39 | $n_{N7}\rightarrow\pi^*_{C6=O5}$ | 18.84 |
| $n_{N5}\rightarrow\pi^*_{C4=O9}$ | 37.42 | | |
| $n_{N3}\rightarrow\pi^*_{C4=O9}$ | 37.36 | | |

The electron occupations of the orbitals involved in donor-acceptor interactions for BA and MNA anions, calculated by NBO analysis are given in Table 5. Note that a light difference in energies (less than 1 kcal mol$^{-1}$) is tolerated in NBO calculations.

**Table 5.** Electron occupancy of orbitals calculated by NBO **method.**

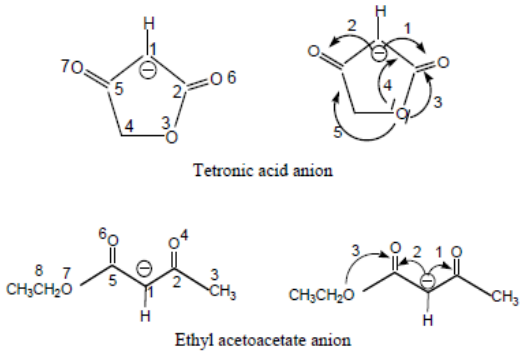
| Compound | Orbital | Occupancy |
|---|---|---|
| Barbituric acid (BA) anion | $n_{C1}$ | 1.379 |
| | $\pi^*_{C2=O8}$ | 0.423 |
| | $\pi^*_{C6=O7}$ | 0.422 |
| | $n_{N3}$ | 1.664 |
| | $n_{N5}$ | 1.663 |
| | $\pi^*_{C4=O9}$ | 0.339 |
| Malonamide (MNA) anion | $n_{C1}$ | 1.372 |
| | $\pi^*_{C2=O4}$ | 0.413 |
| | $\pi^*_{C6=O5}$ | 0.418 |
| | $n_{N3}$ | 1.866 |
| | $n_{N5}$ | 1.882 |

The analysis of electron occupancies shows that the two antibonding $\pi^*_{C=O}$ orbitals are not completely vacant and have an occupancy of 0.42 electrons. The negative charge on carbon atom $C_1$ shows occupancy less than 2 electrons (1.379 and 1.372 electrons for BA and for MNA anions, respectively). The lone pairs $n_N$ of nitrogen atoms are also diminished to 1.663 –1.866 electrons due to charge transfer of the type $n_N\rightarrow\pi^*_{C=O}$. These results confirm the calculated $E^{(2)}$ stabilizations due to donor-acceptor interactions (Table 4).

B3LYP/6-311++G** calculations of the deprotonation free energies give a difference in aqueous phase $\delta\Delta G°= \Delta G°(BA)-\Delta G°(MNA)=15.91$ kcal mol$^{-1}$ indicates the high acidity of BA compared to MNA. This behavior can be explained by the strong delocalization between the lone pairs of nitrogen atoms and the carbonyl group $C_4=O_9$ situated between these two nitrogen atoms. These interactions, denoted designated by numbers 5 and 6 in Scheme 3 are present in BA anion but they are absent in MNA anion. These interactions give a supplementary stabilization of the cyclic anion and consequently justify the high acidity of BA. The $E^{(2)}$ energies are equal to 37.4 kcal mol$^{-1}$ for both $n_{N3}\rightarrow\pi^*_{C4=O9}$ and $n_{N5}\rightarrow\pi^*_{C4=O9}$ donor-acceptor interactions (Table 4). These stabilization interactions are also supported by the strong occupancy of the antibonding orbital $\pi^*_{C4=O9}$ (0.339 electrons, see Table 5).

**Case 3: Tetronic acid/ethyl acetoacetate**

The main stereoelectronic interactions for cyclic TA and acyclic EAA anions are illustrated In Scheme 4 and the corresponding $E^{(2)}$ energies are given in Table 6.




**Scheme 4.** The significant stereoelectronic interactions for TA and EAA anions.

**Table 6.** $E^{(2)}$ energies of the main donor-acceptor interactions for TA and EAA anions.

| Tetronic acid (TA) anion | | Ethyl acetoacetate (EAA) anion | |
|---|---|---|---|
| **Interaction** | **$E^{(2)}$ kcal mol$^{-1}$** | **Interaction** | **$E^{(2)}$ kcal mol$^{-1}$** |
| $n_{C1}\rightarrow\pi^*_{C2=O6}$ | 129.02 | $n_{C1}\rightarrow\pi^*_{C2=O4}$ | 123.61 |
| $n_{C1}\rightarrow\pi^*_{C5=O7}$ | 109.27 | $n_{C1}\rightarrow\pi^*_{C5=O6}$ | 134.11 |
| $n_{O3\,(LP2)}\rightarrow\pi^*_{C2=O6}$ | 70.21 | $n_{O7(LP2)}\rightarrow\pi^*_{C5=O6}$ | 39.57 |
| $n_{O3\,(LP1)}\rightarrow\sigma^*_{C1-C2}$ | 6.80 | | |
| $n_{O3\,(LP1)}\rightarrow\sigma^*_{C4-C5}$ | 1.84 | | |

As it has been discussed above for MA/DEM and BA/MNA couples, the same of donor-acceptor interactions of the type $n_C\rightarrow\pi^*_{C=O}$ are observed for TA/EAA couple. For the TA anion, $E^{(2)}$ =129.02 kcal mol$^{-1}$ for $n_{C1}\rightarrow\pi^*_{C2=O6}$ and 109.27 kcal mol$^{-1}$ for $n_{C1}\rightarrow\pi^*_{C5=O7}$). For EAA anion, $E^{(2)}$=123.61 kcal mol$^{-1}$ for $n_{C1}\rightarrow\pi^*_{C2=O4}$ 134.11 for $n_{C1}\rightarrow\pi^*_{C5=O6}$). TA and EAA anions also exhibited donor-acceptor interactions involving the lone pairs of the ester oxygen atoms and the antibonding $\pi^*$ orbitals of the adjacent carbonyl group. For the TA anion, $E^{(2)}$=70.21 kcal mol$^{-1}$ for $n_{O3(LP2)}\rightarrow\pi^*_{C2=O6}$ interaction. For the EAA anion, $E^{(2)}$ = 39.57 kcal mol$^{-1}$ for $n_{O7\,(LP2)}\rightarrow\pi^*_{C5=O6}$ interaction (Table 6).

The analysis of electronic populations (Table 7) of the TA/EAA couple shows that the antibonding $\pi^*_{C=O}$ orbitals have an occupancy of 0.399 - 0.454 electrons. It is also noted that the occupation of the negative charge $C_1$ is diminished to 1.355 and 1.340 electrons in TA and EAA anions, respectively. The occupancies of the second lone pairs (LP2) of the ester oxygen atoms $n_O$ are also reduced to 1.784 and 1.828 electrons. These results are in accordance with the calculated $E^{(2)}$ stabilizations given in Table 6.

**Table 7.** Electronic occupations of the orbitals calculated by NBO method.

| Compound | Orbital | Occupancy |
|---|---|---|
| Tetronic acid (TA) anion | $n_{C1}$ | 1.355 |
| | $\pi^*_{C2=O6}$ | 0.454 |
| | $\pi^*_{C5=O7}$ | 0.435 |
| | $n_{O3\ (LP2)}$ | 1.784 |
| | $\sigma^*_{C4-C5}$ | 0.060 |
| | $\sigma^*_{C1-C2}$ | 0.052 |
| Ethyl acetoacetate (EAA) anion | $n_{C1}$ | 1.340 |
| | $\pi^*_{C2=O4}$ | 0.399 |
| | $\pi^*_{C5=O6}$ | 0.425 |
| | $n_{O7\ (LP2)}$ | 1.828 |

As it has been observed for MA and BA anions, TA anion also presents important supplementary donor-acceptor interactions of the type $n_O \rightarrow \sigma^*$ between the lone pairs of the ester oxygen and the antibonding σ* orbital. The sum of $E^{(2)}$ energies of $n_{O3(1)} \rightarrow \sigma^*_{C1-C2}$ and $n_{O3(1)} \rightarrow \sigma^*_{C4-C5}$ interactions is equal to 8.64 kcal $mol^{-1}$. The analysis of electron populations shows that the anibonding $\sigma^*_{C1-C2}$ and $\sigma^*_{C4-C5}$ orbitals are not empty and have an occupation of 0.052 and 0.060 electrons, respectively (see Table 7). These donor-acceptor stereo-electronic interactions, which are totally absent in the EAA anion, are the origin of the increase of the stabilization of the cyclic TA anion and consequently may justify explain the notable acidity of TA.

## Conclusion

In this present work, we have presented a theoretical study based on NBO analysis in order to explain the remarkably high acidity of the acids of MA, BA and TA acids compared to their analogous open chains. We have rationalized the role of the stereoelectronic effects on the stability of the studied β-dicarbonyl anions by the quantification of the main donor-acceptor interactions using the $E^{(2)}$ stabilization energies and electron occupations. It turns out that there is several stabilizing interactions which are present in the cyclic β-dicarbonyl anions are completely absent in the corresponding acyclic compounds. These stereoelectronic charge transfer interactions play a determinant role in the stabilization of the conjugate bases of the studied cyclic acids and may explain the origin of their high acidity.

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