energies are quite adequate. Classically,[12] and even contemporaneously,[2a] it is believed that resonance stabilization of the ester function causes it to be less acidic than the corresponding ketone. However, one can also explain the phenomenon in terms of electrostatic interactions. That is, the ester enolate anion experiences some electrostatic repulsion between the developing negative charge and the lone pairs on the ether oxygen. Since the latter are absent in acetone enolate, the anion is easier to form.

In conclusion, there is greater dipole–dipole interaction between the ether oxygen and the carbonyl group in the anti conformation of an acid or ester than in the syn. This difference is significantly reduced in the corresponding enolates. This is the origin of the unusual acidity of Meldrum's acid. Since this is an electrostatic effect, the difference in acidity between syn and anti esters might be reduced in solvents where ion pairing or aggregation occurs.[13] However, in DMSO, where the p$K_a$ measurements were made, there is a good correlation with gas-phase acidities.[14]

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# Acidity of (*Z*)- and (*E*)-Methyl Acetates: Relationship to Meldrum's Acid

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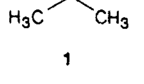
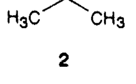
**Abstract:** The difference in acidity between *Z* and *E* rotamers of methyl acetate was calculated via geometry optimization by using the 6-31G* basis set and MP3/6-31G** energy calculations. The loss of a proton from the *E* rotamer was calculated to be easier by 4.7 kcal/mol than for the *Z* rotamer. This difference in acidity easily accounts for the unusual acidity of Meldrum's acid, having a bis(*E*) conformation. The increased acidity results from the change in charge distribution that accompanies the loss of a proton. The ionization of methyl acetate is compared with that of acetic acid, and the origin of their acidity is shown to be the strong polarization inherent in the carbonyl group.

It is known that the *Z* conformers of esters are generally more stable than the *E* conformers. The difference in energy has been measured for methyl formate (4.8 kcal/mol) and for methyl acetate (8.5 kcal/mol).[1] We have shown that it is possible to reproduce these energy differences via ab initio SCF calculations provided that sufficiently large basis sets were used.[2] The difference between the two ester rotamers may well lead to a difference in other properties, such as the acidity. In a continuation of this study, we have examined the acidity of the two rotamers. Evidence that a difference would be found may be found in the work of Arnett and Harrelson,[3] who showed that Meldrum's acid (**1**) is more acidic than dimedone (**2**) despite the normally lower acidity (~4–5 p$K$ units) of esters as compared with ketones. As noted by Arnett, the main difference between Meldrum's acid and ordinary esters is that **1** is required to adopt an *E*-ester conformation.



**1**



**2**

The geometries of the esters and anions were optimized by using the 6-31G* basis set, which is required in order to appropriately reproduce the bond lengths at the carbonyl group.[4] The energies were then calculated by using the 6-31G** basis, which also includes polarization functions at both carbon and hydrogen, and correction for electron correlation was made by using the Møller–Plesset perturbation treatment[5] through the third order (MP3). The energies are given in Table I, and the structural data are shown in Figure 1.

**Table I**

| | 6-31G**/6-31G* | | |
|---|---|---|---|
| compound | RHF | MP2 | MP3 |
| Calculated Energies, hartrees | | | |
| (*Z*)-methyl acetate | −266.846 49 | −267.617 48 | −267.641 67 |
| (*E*)-methyl acetate | −266.831 43 | −267.603 55 | −267.627 87 |
| *Z* anion | −266.205 77 | −266.979 47 | −267.000 48 |
| *E* anion | −266.198 78 | −266.973 80 | −266.994 15 |
| Energy Changes (*Z*–*E* Conformation), kcal/mol | | | |
| methyl acetate | −9.45 | −8.74 | −8.66 |
| anion | −4.39 | −3.56 | −3.97 |
| $\Delta\Delta E$ | −5.06 | −5.18 | −4.69 |

Whereas the MP3/6-31G** energy difference for methyl acetate is 8.7 kcal/mol, that for the anions is only 4.0 kcal/mol, leading to a 4.7 kcal/mol net increase in predicted acidity of the *E* rotamer over that of *Z*. This corresponds to a decrease in p$K_a$ of about 3.4. If one assumes that Meldrum's acid may be considered as a bis(*E* ester), the predicted increase in acidity over

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(1) Blom, C. E.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267.

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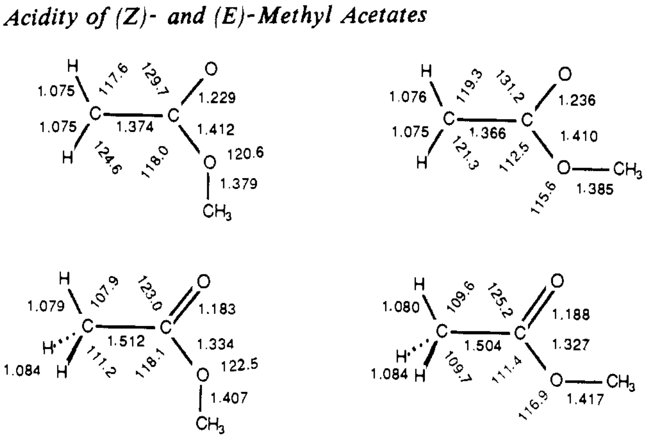


**Figure 1.** Structures of (*E*)- and (*Z*)-methyl acetates and their anions obtained with the 6-31G* basis set. The bond lengths are given in angstroms, and the bond length are given in degrees.

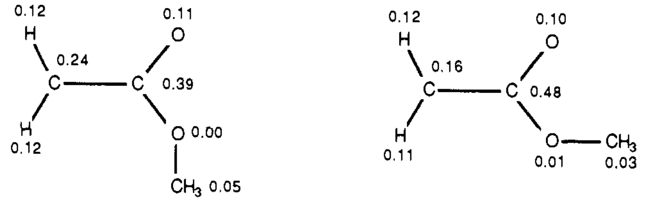
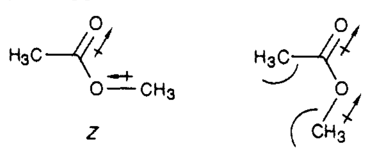


**Figure 2.** Changes in electron population on going from esters to the corresponding anions.

an open-chain ester would be about 7 p*K* units. This is in good agreement with the observations of Arnett and Harrelson.

Why are the *E*-ester rotamers more acidic than the *Z* rotamers? The calculated dipole moments of the two rotamers are 1.99 D (*Z*) and 3.44 D (*E*).[1] The difference in dipole moment results from the different orientations of the C–O bond dipoles; in the *Z* rotamer, they are opposed, whereas in *E* they are additive. Part of the difference in energy between the rotamers is due to the Coulombic attraction of the dipoles in *Z*, which is absent in *E*.[6] It would be reasonable to estimate this energy term as ~4.5 kcal/mol, the difference in energy between the *Z* and *E* forms of methyl formate. The larger energy difference for methyl acetate is due to a steric interaction between the two methyl groups (~4 kcal/mol). The steric interaction is readily seen in the calculated structures, which show greatly increased C–C–O and C–O–C bond angles in the *E* rotamer.



*Z* *E*

When the ester is converted to its anion, the main effect is transfer of negative charge to the carbonyl carbon, reducing the C=O dipole. This may be seen in the changes in electron populations on formation of the anions (Table I, Figure 2). These populations were derived by numerical integration of the charge densities, using the boundary conditions defined by Bader.[7] Although these populations should not be equated with point charges since they are distributed over fairly large volume elements, it may be appropriate to use them in a comparative sense. If one calculates the Coulombic interactions among all of the centers in the esters using the populations, one finds a significantly lower interaction energy in the *Z* ester, as expected. A similar calculation for the anions leads to a slightly lower interaction energy for the *E* anion, suggesting that the difference in Coulombic interactions between the two anions has essentially vanished. A major part of the stabilizing interaction in the *E* anion is the attraction between the partial negative charge at the methylene group and the partial positive charge at the methoxy carbon. The difference in energy between the two anions (Table I) is the same as the steric term for the esters. In view of the rather similar structural deformation in the *E* ester and anion, it is reasonable that the steric component of the energy difference would remain.

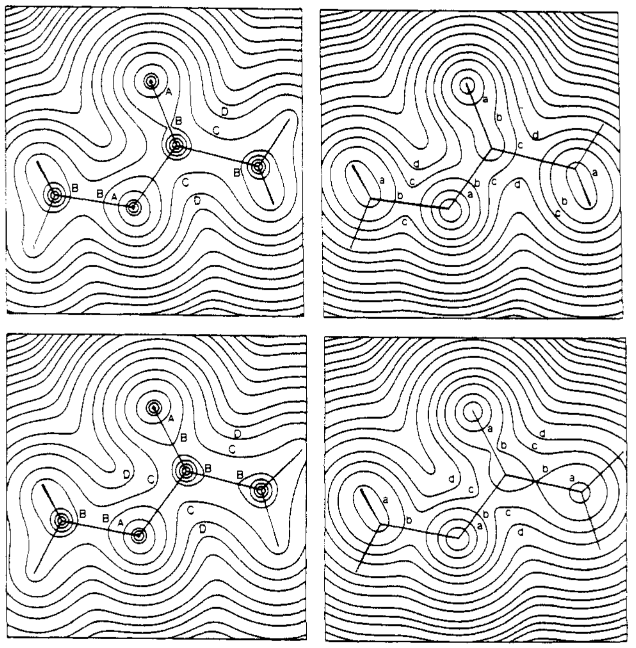


**Figure 3.** Projection density functions ($\int \rho \, d\chi$) for methyl acetate (upper left = total density, upper right = $\pi$ density) and its anion (lower left = total density, lower right = $\pi$ density). The carbonyl group is aligned vertically, and the methoxy group is to the left. Contour values: $A$ = 1.6, $B$ = 0.8, $C$ = 0.4, $D$ = 0.16 e/au$^2$; $a$ = 0.4, $b$ = 0.16, $c$ = 0.08, $d$ = 0.04 e/au$^2$.

**Table II.** Electron Populations[a]

| atom | *Z* | *E* | atom | *Z* | *E* |
|---|---|---|---|---|---|
| Methyl Acetate | | | Methyl Acetate Anion | | |
| C(=O) | 4.090 | 4.096 | C(=O) | 4.572 | 4.485 |
| =O | 9.406 | 9.382 | =O | 9.507 | 9.496 |
| —O— | 9.368 | 9.342 | —O— | 9.362 | 9.344 |
| C(Me) | 5.770 | 5.791 | C($CH_2$) | 5.933 | 6.036 |
| H(Me)[b] | 1.021 | 1.003 | H($CH_2$)[d] | 1.135 | 1.125 |
| H(Me)[c] | 1.026 | 1.039 | H($CH_2$)[e] | 1.135 | 1.157 |
| C(OMe) | 5.223 | 5.213 | C(OMe) | 5.084 | 5.090 |
| H(OMe)[b] | 1.032 | 1.013 | H(OMe)[b] | 1.125 | 1.113 |
| H(OMe)[c] | 1.024 | 1.051 | H(OMe)[c] | 1.081 | 1.095 |
| atom | acetic acid | acetate ion | atom | acetic acid | acetate ion |
| C(=O) | 4.083 | 3.865 | C(Me) | 5.778 | 5.992 |
| =O | 9.405 | 9.500 | H(Me)[b] | 1.107 | 1.047 |
| —O— | 9.340 | 9.505 | H(Me)[c] | 1.021 | 1.046 |
| | | | H(OH) | 0.343 | |

[a] The total electron populations are given. To obtain the valence electron populations, subtract 2.000 from the carbon and oxygen populations. [b] Unique hydrogen. [c] One of a pair of equivalent hydrogens. [d] Hydrogen syn to the carbonyl oxygen. [e] Hydrogen anti to carbonyl oxygen.

The lack of a strong charge shift to the carbonyl oxygen on ionization may at first appear surprizing. The electron density projection plots that have been developed by Streitwieser[8] are especially valuable in visualizing the charge distributions. Here, all of the charge density above and below the molecular plane at a given point is integrated and assigned to that point. This is done for a reasonably large grid (101 × 101 in the present study) and

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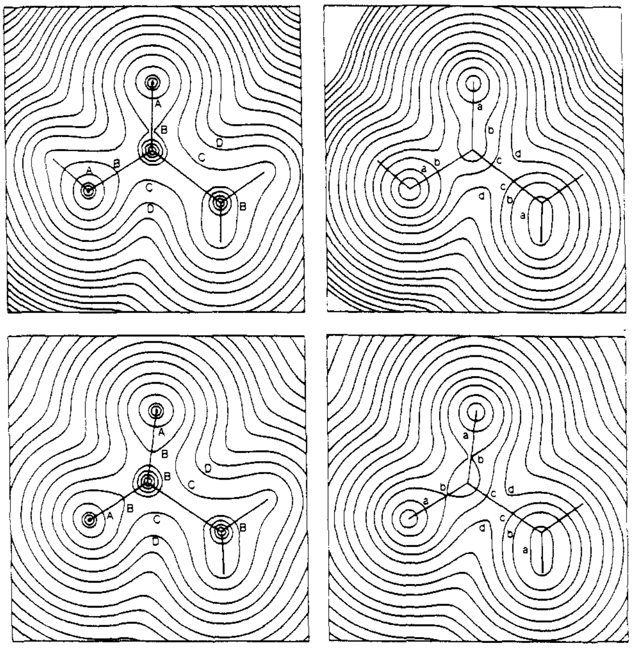

**Figure 4.** Projection density functions for acetic acid (upper left = total density, upper right = $\pi$ density) and acetate ion (lower left = total density, lower right = $\pi$ density). The contour values are the same as for Figure 3.

the result is presented as a contour plot. Plots of this type are shown for (*Z*)-methyl acetate and its anion in Figure 3. The corresponding plots for the *E* ester and anion appear quite similar. In the plots, one might first note how the oxygens dominate the charge distribution. The carbonyl carbon has been stripped of much of its valence electron distribution, and this agrees well with the strong polarization found in the population analysis.

When the ester and anion are compared, it will be seen that the total density contours are not much different. One might expect the main change to be found with the $\pi$ (out-of-plane) electrons, and their projected densities also are shown in Figure 3. Contrary to common expectation, there is relatively little shift in $\pi$ density to the carbonyl oxygen on going from the ester to the anion. One must conclude that the origin of the acidity of the esters is the strong polarization of the carbonyl group caused by its oxygen.

It is interesting to compare the results for the ester and its anion with the acetic acid and acetate ion, since the process involved is essentially the same and since the electron populations for methyl acetate and acetic acid are essentially the same (Table II). Charge density projection plots for acetic acid and acetate ion are given in Figure 4. If one were to overlay the total density plots for the acid and the ion, one would find that the locations of the oxygens and the methyl group are essentially unchanged on ionization; only the carbonyl carbon moves. Again, the contours do not change much on going from the acid to the anion. This also is seen on examining just the $\pi$ charge density plot. There is not a large shift in charge to the carbonyl oxygen on ionization. These results are completely in accord with the conclusions of Siggel and Thomas[9] that the difference in acidity between ethanol and acetic acid results from the polarization of the carbonyl group in the acid.

One may also note that whereas the electron population at the carbonyl carbon of the esters increases on ionization, that for acetic acid decreases. The latter is what one might expect for an allyl anion of the type O–C–O. Here one $\pi$ MO will have a node at the carbon, and the other will have a relatively small coefficient at carbon because of the electronegativity of the adjacent oxygens. In addition, the electron population at the hydroxy hydrogen is quite small, and so there is not a large amount of charge to be distributed after ionization. On the other hand, an allyl anion of the type O–C–C would be expected to have an increased population at the central carbon because the node in the higher energy $\pi$ MO will be between the carbon and oxygen, giving the former a significant coefficient. The terminal carbon will be electropositive with respect the central carbon and should donate charge density both via the $\sigma$ and $\pi$ MOs. Considerations of these types are important for many carbon acids, and we shall subsequently report similar studies of a wide range of these acids.

**Acknowledgment.** The calculations were carried out with GAUSSIAN-82.[10] The post-Hartree–Fock calculations were carried out at the Pittsburgh Supercomputing Center with the aid of a grant of computer time from that center. The projection density functions were calculated with a CSPI array processor, which was provided by a DOD instrument grant. The electron populations were calculated with PROAIMS.[11] The investigation was supported by NIH Grant 1GM11629.

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# Benzyne, Cyclohexyne, and 3-Azacyclohexyne and the Problem of Cycloalkyne versus Cycloalkylideneketene Genesis

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*Contribution from the Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Queensland, Australia 4067.* *Received July 29, 1987*

**Abstract:** Benzyne, cyclohexyne, and 3-azacyclohexyne have been obtained by flash vacuum pyrolysis of phthalic anhydride, 4-cyclopentylidene-3-methylisoxazol-5(4*H*)-one (**34**), and 3-methyl-4-(2-pyrrolidinylidene)isoxazol-5(4*H*)-one (**37**), respectively, isolated at 77 K and observed by IR spectroscopy. Trapping and fragmentation reactions are described, and the implications for the mechanism of benzyne formation from phthalic anhydride via cyclopentadienylideneketene (**9**) are discussed.

The formation of benzyne (**1**) in the high-temperature pyrolyses[2] of phthalic anhydride (**3**) and benzocyclobutenedione (**4**) continues to attract vigorous attention, particularly because of the possibility of interconversion of benzyne and cyclopentadienylidenecarbene

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