H, 5.61; N, 5.20. Found: C, 89.36; H, 5.64; N, 5.38. Benzophenone cyanohydrin was partially decomposed to benzophenone on the silica gel column.

In the absence of benzene, no fluorene compound was formed in the presence of TFSA even at room temperature. The only products were benzophenone and benzophenone cyanohydrin. 9-Cyanofluorene was not formed from the cyanohydrin when the catalytic acid was replaced with SbF_5-FSO_3H (1:1).

Formation and Reaction of Cyanodiphenylmethyl Cation (31) Prepared by Silver Ion Assisted Ionization of Cyanodiphenylmethyl Chloride (30). A solution of cyanodiphenylmethyl chloride (**30**) in 2.4 mL of dry benzene was added in one portion to a solution of 158.9 mg of TfOAg (1.1 equiv with respect to the chloride) in 2 mL of dry benzene at 0-5 °C with stirring. After 4 h at that temperature, the solution was poured into ice-water and worked up as usual. The crude products were flash chromatographed (CH_2Cl_2-*n*-hexane 2:3) to give a triphenylmethyl cyanide (**29**; 111.7 mg, yield 85%). These results are the same as those in the reactions catalyzed by TFSA, suggesting that the electrophilic reaction of cyanodiphenylmethyl cation with benzene does not require a strong acid. In the absence of benzene, the stable red solution was obtained even at 0 °C. NMR spectroscopic measurements indicated the formation of cyanodiphenylmethyl cation (**31**). The ^{13}C NMR absorptions of **31** in TFSA at -30 °C were as follows: 168.5 (s, C^+), 153.3 (d, C_p), 146.0 (d, C_o, br), 138.4 (s, C_{ipso}), 133.57 (d, C_m), 111.8 (s, CN). These spectroscopic results are consistent with previous spectra obtained in other acid systems.[10b]

Acid-Catalyzed Reactions of (Trifluoromethyl)diphenylmethanol (33) in the Presence of Benzene. To an ice-cooled solution of 0.44 mL (10 equiv) of TFSA in 4.4 mL (100 equiv) of dry benzene was added 127.5 mg (ca. 0.5 mmol) of **33** in portions. Stirring was continued at 0-5 °C for 15 min, followed by the usual aqueous workup. Evaporation of the solvent and flash column chromatography with *n*-hexane as the eluent gave 41.7 mg of (trifluoromethyl)triphenylmethane (**34**), 27.4 mg of fluorene dimer **35**, and 54.6 mg of fluorene trimer **36**. The dimeric and trimeric products (**35**, **36**) were formed by the intermolecular electrophilic reactions of the diphenylmethyl cation with the formed fluorene.

When the reaction was catalyzed with a less acidic system (TFSA-TFA 1:4 v/v 0-5 °C, 1 h), the yields of products were as follows: **34**, 43%; **35**, 6%; **36**, 31%. The increase in the yield of **34** indicated that the cyclization reaction to fluorenes does not require a strong acid catalyst. **34**: mp 164 °C (recrystallized from *n*-hexane); mass spectrum, *m/e* 312 (M^+). **35**: viscous oil; HRMS calcd for $C_{28}H_{18}F_6$ 468.13134, found 468.1304; ^1H NMR 7.80-7.48 (m, 4 H), 7.48-6.92 (m, 14 H), 4.60 (q, 1 H, J_{HF} = 9.76 Hz). **36**: mp 163-163.5 °C (recrystallization from *n*-hexane); HRMS calcd for $C_{42}H_{27}F_9$ 702.197 01, found 702.1963; ^1H NMR 7.80-7.48 (m, 4 H), 7.48-6.92 (m, 24 H), 4.60 (q, 1 H, J_{HF} = 9.80 Hz).

Reaction of (Trifluoromethyl)diphenylmethanol (33) in TFSA. To 4.4 mL (500 equiv) of TFSA cooled to -53 °C in a dry ice-methanol bath was added **33** in portions with vigorous stirring. The resultant red solution was stirred for 30 min at -53 °C before the usual aqueous workup. The crude mixture was flash chromatographed with *n*-hexane as the eluent to give 7.3 mg (3%) of 9-(trifluoromethyl)fluorene (**39**), 8.3 mg (3%) of fluorene dimer **35**, and 75.3 mg (32%) of fluorene trimer **36**. The product **39** was identical with an authentic sample in terms of NMR and IR spectra. **39**: HRMS calcd for $C_{14}H_9F_3$ 234.06543, found 234.0654; ^1H NMR: 7.82-7.67 (5 H, m), 7.55-7.28 (5 H, m), 4.60 (1 H, q, J_{HF} = 9.80 Hz).

Reaction of (Trifluoromethyl)diphenylmethyl Cation (38) Prepared by Silver Ion Assisted Ionization of (Trifluoromethyl)diphenylmethyl Bromide (37). A solution of the bromide **37** (314 mg, 1 mmol) in 2 mL of CH_2Cl_2 was added in one portion to a solution of AgOTf (489.2 mg, 1.9 equiv) in 4 mL of CH_2Cl_2 with vigorous stirring at -50 °C in a dry ice-ethanol bath. After being stirred at -50 °C for 1 h, the resulting red solution was poured into ice and water and extracted with CH_2Cl_2. The residue was flash chromatographed with CH_2Cl_2-*n*-hexane (1:8) to give fluorene trimer **36** (80.7 mg, 35% yield) and undefined fluorene derivatives.

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Theoretical Elucidation of the Origin of the Anomalously High Acidity of Meldrum's Acid

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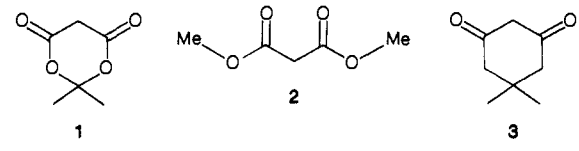
Abstract: The acidity of methyl acetate in syn and anti conformations has been investigated with ab initio calculations and the 3-21G, 6-31G*, and 6-31+G* basis sets. The deprotonation of the anti conformation requires 5.4 kcal/mol less energy than deprotonation of the syn conformation. The constraint of two ester groups in a dilactone to anti conformations should decrease the deprotonation energy by about 11 kcal/mol, essentially the amount by which Meldrum's acid is more acidic than malonic ester in DMSO solution. The higher acidity of the anti conformation is attributed to electrostatic (dipole-dipole) repulsion effects. An electrostatic effect, rather than the usually invoked resonance effect, is also proposed to be responsible for the lower acidity of esters as compared with ketones.

Arnett and Harrelson recently studied a variety of systems in order to understand the unusually high acidity of Meldrum's acid[1] (**1**). This dilactone has a considerably higher acidity (pK_a 7.3) than acyclic analogues such as dimethyl malonate (**2**; pK_a 15.9), or even the diketone analogue **3** (pK_a 11.2). These pK_a's were all measured in DMSO, in which the acidities are uncomplicated by aggregation or counterions. Arnett and Harrelson proposed that the anomalously high acidity of **1** is connected to the he unfavorable anti conformations that the ester groups are forced to adopt in Meldrum's acid. However, Arnett and Harrelson left a tantalizing sense of mystery about the origin of the effect.[2a]



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(1) (a) Meldrum, A. N. *J. Chem. Soc., Trans.* **1908**, *93*, 589. (b) Davidson, D.; Bernhard, S. A. *J. Am. Chem. Soc.* **1948**, *70*, 3426. (c) Arnett, E. M.; Harrelson, J. A. *Gazz. Chim. Ital.*, in press. (d) Pfluger, C. E.; Boyle, P. D. *J. Chem. Soc., Perkin Trans. 2*, 1985, 1547.

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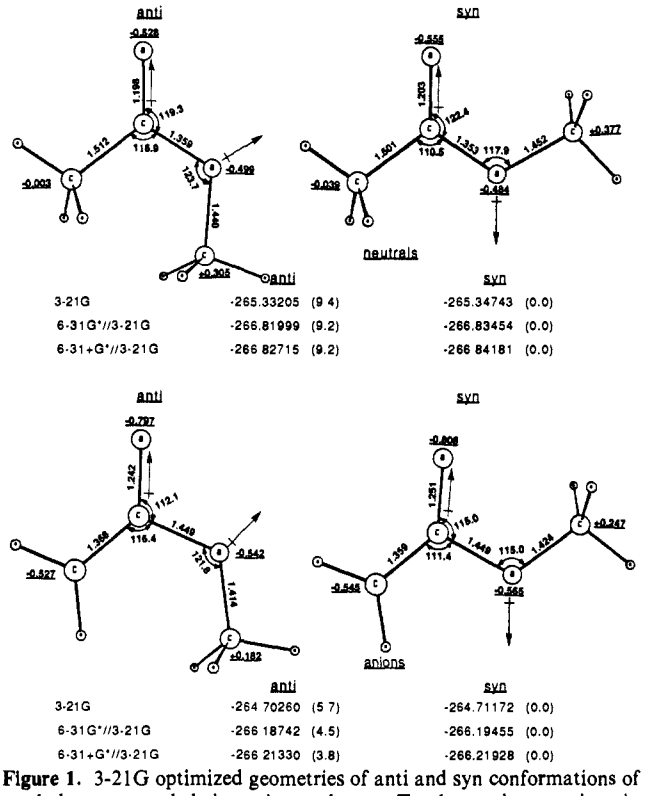

Figure 1. 3-21G optimized geometries of anti and syn conformations of methyl acetate and their conjugate bases. Total energies are given in hartrees and relative energies are given in parentheses in kilocalories per mole. Angles are in degrees, and bond lengths are in angstroms. The underlined numbers are Mulliken charges on oxygens or methyl groups according to 6-31+G*//3-21G calculations.

The special effects in Meldrum's acid are energetically enormous: in DMSO solution at 25 °C, deprotonation of **1** is 11.6 kcal/mol less endothermic than deprotonation of **2**. The conformational differences between **1** and **2** were suggested to influence stereoelectronic factors, inductive effects, or dipole interactions in some way, leading to the acidity enhancement of **1**. Arnett offered the source of these large effects as "a worthy target for theoretical elucidation".[2] We have now completed theoretical studies that provide an explanation of these effects.[3]

Results and Discussion

The structures of the anti and syn conformations of methyl acetate and the corresponding conjugate bases were optimized with ab initio quantum mechanical calculations and the 3-21G basis set.[4] The energies of these structures were then reevaluated with the larger 6-31G* and 6-31+G* basis sets. The last basis set has both polarization functions and diffuse functions on heavy atoms. The diffuse functions are necessary for the proper treatment of anions. As described later, the largest basis set used here gives reasonable relative acidities. The calculations are summarized in Figure 1.

The syn conformations of both ester and anion are more stable than the anti conformations. For methyl acetate, the syn conformer is calculated to be 9.2 kcal/mol more stable than the anti, whereas the experimental difference is 8.5 ± 1 kcal/mol.[6] The perpendicular conformation, which is a local energy maximum, is 10–15 kcal/mol higher in energy.[6]

Table I. Experimental ΔH_{acid} and 6-31+G*//3-21G Calculated ΔE for Deprotonation of Acetone and Methyl Acetate in Gas Phase[a]

	CH_3COCH_3	$CH_3CO_2CH_3$
exptl[11] ΔH_{acid}	368.8 (0.0)	371.0 (2.2)
calcd ΔE	388.2 (0.0)	390.6 (2.4)

[a] Deprotonation energies are given in kilocalories per mole. Relative energies are given in parentheses.

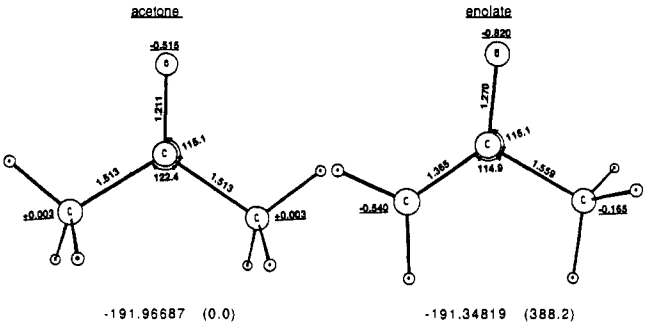

Figure 2. 3-21G optimized geometries of acetone and its enolate. Energies are given in hartrees according to 6-31+G*//3-21G calculations. Relative energies are given in parentheses in kilocalories per mole. Angles are in degrees, and bond lengths are in angstroms. The underlined numbers are Mulliken charges on oxygens or methyl groups.

The energy difference between the syn and anti conformations of an ester anion is 3.8 kcal/mol at the best level evaluated, which is smaller by about 5 kcal/mol than the energy difference between the neutral ester conformations. The conversion of two syn esters of malonic ester to the anti lactones of Meldrum's acid is calculated to increase acidity by 10 kcal/mol, essentially the amount observed experimentally. In explaining the large "extra acidity" of Meldrum's acid, Arnett cited Huisgen's observation that cyclic lactones are destabilized relative to acyclic analogues (3.8 kcal/mol).[5b] There is ample evidence that esters prefer the syn conformation over the anti.[2,4-9] A variety of explanations have been offered. We subscribe to the careful analysis of Roos et al.,[9] who deduced that the syn conformation is preferred because of the greater electrostatic of dipole–dipole repulsions in the anti conformation.[6-8]

The syn conformation has those dipole moment components for the carbonyl groups and ether lone pairs, which are depicted qualitatively by the arrows in Figure 1. In the syn conformation, these point in opposite directions, while in the anti conformation these point in the same direction, leading to the destabilization of the anti ester. In the ester enolate ions, the dipole moment component generated by the enolate moiety is reduced relative to that of an isolated carbonyl group, since the enolate has appreciable negative charge at the methylene group. Consequently, there is a reduced electrostatic preference for the syn conformation in the enolate. Nevertheless, the syn conformation is still more stable than the anti, because the oxygen of the enolate is more negative than the methylene terminus, as indicated by the atomic charges shown in Figure 1.

In order to verify that the 6-31+G* level is adequate for the calculation of relative acidities, we also calculated the deprotonation energy of acetone (Table I, Figure 2). The deprotonation energies calculated are larger than experimental,[11] but the relative

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(5) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983.

(6) Blom, C. H.; Günthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267.

(7) (a) Huisgen, R. *Angew. Chem.* **1987**, *69*, 341. (b) Huisgen, R.; Ott, H. *Tetrahedron* **1959**, *6*, 253. (c) Edward, J. T. *Chem. Ind. (London)* **1955**, 1102–1104. (d) Jefrey, G. A.; Pople, J. A.; Radom, L. *Carbohydr. Res.* **1972**, *25*, 117–131.

(8) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14 and references therein.

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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 pK_a measurements were made, there is a good correlation with gas-phase acidities.[14]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to Frank Jensen for calling our attention to this problem.

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(12) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955.
(13) Studies of solvation are under way in collaboration with Professor William L. Jorgensen.
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Acidity of (*Z*)- and (*E*)-Methyl Acetates: Relationship to Meldrum's Acid

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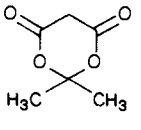
Abstract: The difference in acidity between *Z* and *E* rotamers of methyl acetate was calculated via geometry optimization by using the 6-31G* basis set and MP3/6-31G** energy calculations. The loss of a proton from the *E* rotamer was calculated to be easier by 4.7 kcal/mol than for the *Z* rotamer. 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.



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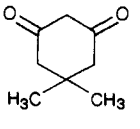

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The geometries of the esters and anions were optimized by using the 6-31G* basis set, which is required in order to appropriately reproduce the bond lengths at the carbonyl group.[4] The energies were then calculated by using the 6-31G** basis, which 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

compound	6-31G**/6-31G* 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 pK_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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