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# Thermochemistry of (*E*)- and (*Z*)-disubstituted alkene species: a combined experimental and theoretical investigation of isomeric dimethyl fumarate and dimethyl maleate

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The first unequivocal thermochemical/calorimetric determination of the enthalpies of combustion, phase change, and formation of a pair of (*E*)- and (*Z*)-disubstituted olefins of the type XCH=CHX, where X is an electron withdrawing group, is reported in this paper for the isomeric species dimethyl fumarate and dimethyl maleate (X = $COOCH_3$). The corresponding density functional calculations, corrected for vibrational and thermal effects, confirm that the former isomer is more stable by some 30 kJ $mol^{-1}$.

## Introduction

Olefins are a well known class of organic compounds and the >C=C< moiety is an important functional group.[1] It is unequivocal that for olefins of the structural type X–CH=CH–X, the (*E*)-isomer is thermochemically more stable than its (*Z*)-counterpart when X = alkyl,[2] whether it be for X = $CH_3$,[3] $(CH_3)_3C$[4] or $(CH_3)_3CCH_2$.[5] Steric constraints are not sufficient to determine the isomeric character of the olefin, for when X has lone pairs, whether it be $CH_3O$[6a] and F,[6b] or I[7], the (*Z*)-isomer gains stability so that it is either more stable or of comparable stability to the corresponding (*E*)-isomer. All of the aforementioned X substituents are π-donors; what if the substituents are not? For X = $C_6H_5$, electronically considered as both a donor and acceptor, the (*E*)-isomer is unequivocally the more stable. However, the phenyl group is large. For the smaller and likewise electronically "ambivalent" X = CH=$CH_2$,[8] the (*E*)-isomer is more stable (error bars allow for equal stability) while for the weakly electron withdrawing X = C≡CH,[9] the (*E*)-isomer is more stable as well. What about X being a definitively electron withdrawing group? The thermochemical literature is muddy, if not mute: while the enthalpies of formation of both the (*E*)- and (*Z*)-isomeric compounds X–CH=CH–X, where X = COOH species, fumaric and maleic acids, have been measured, the presence of intramolecular hydrogen bonding for only the latter isomer confounds simple interpretation of the results (ignoring error bars, the gaseous (*Z*)-isomer is more stable).[10] In addition, the possibility of thermally induced dehydration of maleic acid complicates interpretation of the sublimation enthalpy. While it is tempting to suggest that any species for which X is an electron-withdrawing group would be more stable as its (*E*)-isomer for both size and electronic reasons (*e.g.* due to repulsion of the negative X groups), such logic would naturally apply to species such as the aforementioned 1,2-dimethoxyethylene and we remind the reader that this conclusion is wrong here. So, what X do we choose and what do we find?

In the current study, we provide an answer to this question. What follows is the report of our study of the thermochemistry of the two compounds with X = $COOCH_3$, the isomeric dimethyl fumarate (DMeF) and dimethyl maleate (DMeM) using a combination of experimental thermochemical determinations and high-level theoretical calculations of the standard enthalpies of formation in the gas phase.

In the experimental part of this paper, we report the standard molar enthalpies of formation of dimethyl fumarate and dimethyl maleate in the gas phase. We have combined the results of measurements of combustion energies using a static bomb calorimeter and the values for the enthalpies of sublimation or vaporization of the compounds measured using a Calvet microcalorimeter.

The most stable geometries of the two isomers were obtained using density functional theory with the B3LYP functional and three basis sets: 6-31G*, 6-311G** and cc-pVTZ. The values of the gas phase enthalpies of formation, $\Delta_f H_m°$ (g), for the two isomers were calculated through a bond separation isodesmic reaction. There is a good agreement between the calculated and experimental enthalpies of formation. These calculations were also used to gain a better understanding of the relationship between structure and the relative thermochemical stability of the two isomers.

## Results and discussion

### Experimental results

Results for a typical combustion experiment of each compound are given in Table 1, where $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g. Combustion experiments were made in oxygen at $p$ = 3.04 MPa, with 1.00 $cm^3$ of water added to the bomb: $\Delta U_\Sigma$ is the correction to the standard state. The remaining quantities are as previously described.[11] For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u° = -16250$ J $g^{-1}$.[12] The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on $-59.7$ kJ $mol^{-1}$[13] for the molar energy of formation of 0.1 mol $dm^{-3}$ $HNO_3$(aq) from $N_2$, $O_2$, and $H_2O$(l). As samples were ignited at $T$ = 298.15 K,

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon_{\mathrm{cal}} + \Delta m(\mathrm{H_2O}) \times c_p(\mathrm{H_2O,\,l}) + \varepsilon_{\mathrm{f}}\}\,\Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}} \quad (1)$$

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where $\Delta U$(IBP) is the energy associated with the isothermal bomb process, $\varepsilon_f$ is the energy of the bomb contents after ignition and $\Delta T_{ad}$ is the adiabatic temperature rise. The individual results of all the combustion experiments, together with the mean value and its standard deviation, are given for each compound in Table 2. Table 3 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U_m°$ (cr, l) and $\Delta_c H_m°$ (cr, l), and the standard molar enthalpies of formation of the compounds in the condensed phase $\Delta_f H_m°$ (cr, l) at 298.15 K. In accordance with customary thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, twice the overall standard deviation of the mean and include the uncertainties in calibration[14] and in the values of auxiliary quantities. To derive $\Delta_f H_m°$ (cr, l) from $\Delta_c H_m°$ (cr, l) the standard molar enthalpies of formation of $H_2O$(l) and $CO_2$(g) at $T = 298.15$ K, −(285.830 ± 0.042) kJ $mol^{-1}$ [15] and −(393.51 ± 0.13) kJ $mol^{-1}$,[15] respectively, were used.

Measurements of the enthalpies of sublimation and vaporization $\Delta_{cr,l}^{g} H_m°$ are given in Table 4 with uncertainties of twice the standard deviation of the mean. The derived enthalpies of formation in both the condensed and gaseous phases for the two compounds are summarized in Table 5.

The enthalpy of fusion of the crystalline dimethyl fumarate, (32.40 ± 0.15) kJ $mol^{-1}$, at the temperature of fusion ($T$ = 375.28 ± 0.08 K) was derived from the DSC experiments. The uncertainties assigned to these results are twice the standard deviation of the mean of six independent runs. This result is in perfect agreement with the literature value of 35.15 kJ $mol^{-1}$ at $T = 375$ K.[16,17]

Published vapor pressure data exist from which one can derive the values of the vaporization enthalpies for both dimethyl fumarate ($\Delta_l^g H_m° = 53.8$ kJ $mol^{-1}$, at $T = 376$ K; range $T$ = 361 to 466 K) and dimethyl maleate ($\Delta_l^g H_m° = 52.0$ kJ $mol^{-1}$, at $T$ = 400 K, range $T$ = 385–421 K).[18] For dimethyl fumarate, considering the literature value of the vaporization enthalpy = 53.8 kJ $mol^{-1}$ at $T$ = 376 K, and the value of the enthalpy of fusion = (32.40 ± 0.15) kJ $mol^{-1}$ at $T$ =375.28 K, we obtain a value of 86.2 kJ $mol^{-1}$ for the enthalpy of sublimation at $T = 376$ K. This value can be corrected to 298.15 K, using the equation

$$\Delta_{cr}^{g} H_m^{\circ}(298.15\ \text{K}) = \Delta_{cr}^{g} H_m^{\circ}(376\ \text{K}) + \int_{376}^{298.15} \left[ C_{p,m}^{\circ}(\text{g}) - C_{p,m}^{\circ}(\text{cr}) \right] \text{d}T \quad (2)$$

where

$$C_{p,m}^{\circ}(\text{g})/\text{J mol}^{-1}\ \text{K}^{-1} = -\frac{1.288T^2}{10^4} + 0.452T + 34.42 \quad (3)$$

was derived from statistical thermodynamics[19] using the vibrational frequencies derived from the B3LYP/6-31G* calculations, and $C_{p,m}°$ (cr) = 199.2 J $mol^{-1}$ $K^{-1}$ [17] was taken as constant in the range $T$ = 298 to 376 K. The literature value for the enthalpy of sublimation of dimethyl fumarate corrected to $T = 298.15$ K is $\Delta_{cr}^{g} H_m° = 88.3$ kJ $mol^{-1}$, in perfect agreement with our experimental value of $\Delta_{cr}^{g} H_m°$ = (88.4 ± 1.6) kJ $mol^{-1}$.

For dimethyl maleate the literature value[18] for the enthalpy of vaporization, $\Delta_l^g H_m° = 52.0$ kJ $mol^{-1}$ at $T$ = 400 K, is obviously not in agreement with our value, (64.4 ± 1.6) kJ $mol^{-1}$ at $T = 298.15$ K. We are unable to explain this discrepancy.

## Theoretical results

**Optimized geometries.** The equilibrium geometries obtained by the DFT/B3LYP/6-311G** method are shown in Table 6, where, for the sake of conciseness, the geometrical parameters relating to the C–H bonds have been omitted. Fig. 1 displays the

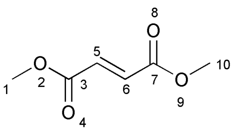

**Fig. 1** Atomic numbering scheme of the isomers (dimethyl fumarate shown).

**Table 1** Typical combustion experiments at $T = 298.15$ K

| | DMeF | DMeM |
|---|---|---|
| $m(CO_2$, total)/g | 1.62671 | 1.83284 |
| $m$(cpd)/g | 0.88442 | 0.92611 |
| $m'$(fuse)/g | 0.00392 | 0.00392 |
| $m''$(melinex)/g | — | 0.05666 |
| $\Delta T_{ad}$/K | 1.06259 | 1.21670 |
| $\varepsilon_f$/J $K^{-1}$ | 16.43 | 16.65 |
| $\Delta m(H_2O)$/g | 0.0 | 0.0 |
| $-\Delta U$(IBP)/J | 17022.81 | 19492.54 |
| $-\Delta U$(melinex)/J | — | 1297.58 |
| $-\Delta U$(fuse)/J | 63.66 | 63.66 |
| $-\Delta U(HNO_3)$/J | 0.60 | 1.06 |
| $-\Delta U$(carbon)/J | 0.00 | 0.00 |
| $\Delta U$(ign)/J | 1.19 | 0.76 |
| $-\Delta U_\Sigma$/J | 13.39 | 15.43 |
| $-\Delta_c u°$/J $g^{-1}$ | 19159.63 | 19560.11 |

**Table 2** Individual values of the massic energy of combustion at $T = 298.15$ K

| $-\Delta_c u°$/J $g^{-1}$ | |
|---|---|
| DMeF | DMeM |
| 19185.65 | 19529.29 |
| 19159.63 | 19530.90 |
| 19171.89 | 19560.11 |
| 19193.11 | 19543.38 |
| 19176.07 | 19571.49 |
| 19157.39 | 19577.93 |
| 19168.23 | 19557.40 |
| | 19558.23 |
| | 19555.13 |
| $-\langle\Delta_c u°\rangle$/J $g^{-1}$ | |
| 19173.1 ± 4.9 | 19553.8 ± 5.5 |

**Table 3** Derived standard ($p°$ = 0.1 MPa) molar energies and enthalpies of combustion and enthalpies of formation at $T = 298.15$ K

| | $-\Delta_c U_m°$(cr, l)/kJ $mol^{-1}$ | $-\Delta_c H_m°$(cr, l)/kJ $mol^{-1}$ | $-\Delta_f H_m°$(cr, l)/kJ $mol^{-1}$ |
|---|---|---|---|
| DMeF (cr) | 2763.4 ± 1.8 | 2763.4 ± 1.8 | 741.0 ± 2.0 |
| DMeM (l) | 2818.2 ± 1.9 | 2818.2 ± 1.9 | 686.2 ± 2.1 |

**Table 4** Standard molar ($p°$ = 0.1 MPa) enthalpies of sublimation and vaporization at $T = 298.15$ K

| | No. of expts | $T$/K | $\Delta_{cr,l,298.15\,K}^{g,T} H_m°$(g)/kJ $mol^{-1}$ | $\Delta_{298.15\,K}^{T} H_m°$(g)/kJ $mol^{-1}$ | $\Delta_{cr,l}^{g} H_m°$(298.15 K)/kJ $mol^{-1}$ |
|---|---|---|---|---|---|
| DMeF (cr) | 6 | 376 | 102.6 ± 1.6 | 14.2 | 88.4 ± 1.6 |
| DMeM (l) | 6 | 377 | 78.8 ± 1.6 | 14.4 | 64.4 ± 1.6 |

**Table 5** Derived standard ($p° = 0.1$ MPa) molar enthalpies of formation in the condensed and gas phases at $T = 298.15$ K

| | $-\Delta_f H_m°(\text{cr, l})/\text{kJ mol}^{-1}$ | $\Delta_{\text{cr,l}}^{\text{g}} H_m°/\text{kJ mol}^{-1}$ | $-\Delta_f H_m°(\text{g})/\text{kJ mol}^{-1}$ |
|---|---|---|---|
| DMeF (cr) | 741.0 ± 2.0 | 88.4 ± 1.6 | 652.6 ± 2.6 |
| DMeM (l) | 686.2 ± 2.1 | 64.4 ± 1.6 | 621.8 ± 2.6 |

**Table 6** Bond lengths (Å) and bond angles (°) of the isomers using the calculated B3LYP/6-311G** method

| | DMeF | DMeM |
|---|---|---|
| 1–2 | 1.44 | 1.44 |
| 2–3 | 1.35 | 1.34 |
| 3–4 | 1.21 | 1.21 |
| 3–5 | 1.49 | 1.49 |
| 5–6 | 1.33 | 1.33 |
| 6–7 | 1.49 | 1.49 |
| 7–8 | 1.21 | 1.21 |
| 7–9 | 1.35 | 1.34 |
| 9–10 | 1.44 | 1.44 |
| 1–2–3 | 115.6 | 115.3 |
| 2–3–4 | 124.0 | 124.2 |
| 2–3–5 | 110.3 | 113.0 |
| 3–5–6 | 120.9 | 128.1 |
| 5–6–7 | 120.9 | 128.1 |
| 6–7–8 | 125.7 | 122.7 |
| 6–7–9 | 110.3 | 113.0 |
| 7–9–10 | 115.6 | 115.3 |
| 1–2–3–4 | 0.0 | 3.7 |
| 1–2–3–5 | 180.0 | −179.0 |
| 2–3–5–6 | 180.0 | 41.8 |
| 4–3–5–6 | 0.0 | −140.8 |
| 3–5–6–7 | 180.0 | −0.9 |
| 5–6–7–8 | 0.0 | −140.5 |
| 5–6–7–9 | 180.0 | 42.1 |
| 6–7–9–10 | 180.0 | −179.0 |
| 8–7–9–10 | 0.0 | 3.6 |

atomic numbering scheme used. The (*E*)-isomer is predicted to adopt a planar conformation while in the (*Z*)-isomer the two $COOCH_3$ groups are rotated in opposite directions about the bond connecting them to the central C=C double bond, thus leading to a conformation which is considerably non-planar. This loss of planarity is likely to hinder the extended electronic delocalization that, otherwise, would occur between the two $COOCH_3$ groups, through the central C=C double bond.

Total energies, identified by the subscripts B3LYP/6-31G*, B3LYP/6-311G**, and B3LYP/cc-pVTZ, and the zero-point vibrational energies and thermal energy corrections are reported in Table 7 for the two isomers.

It can be observed from the results in Table 7 that the (*E*)-isomer is predicted, by both calculations, to be more stable than the (*Z*)-isomer. The energy difference between both isomers, about 31.5, 30.7 and 29.1 kJ mol$^{-1}$, obtained, respectively, from the B3LYP/6-31G*, B3LYP/6-311G** and B3LYP/cc-pVTZ energies, is in very good agreement with the difference in the experimental standard enthalpies of formation, which amounts to (30.8 ± 3.7) kJ mol$^{-1}$.

We believe that the more effective electronic delocalization in the (*E*)-isomer must be responsible for a fraction of the difference in stability observed between the two isomers. However, more careful calculations, based on a topological analysis of the electronic density in the framework of the atoms in molecules (AIM) theory[20] allowed the characterization of the bond order of the relevant bonds of both isomers, leading to results that indicate that the different effectivity of the extended electronic delocalization must have, at most, a minor effect on the total stability difference observed. Indeed, only small variations in the bond orders have been observed between the two isomers. Larger variations in the bond orders are observed for the central C=C double bond (1.99 in the (*E*)-isomer and 1.79 in the (*Z*)-isomer) and for the bonds connecting the CO-$OCH_3$ groups to the central bond (1.22 in the (*E*)-isomer and 1.19 in the (*Z*)-isomer). Thus, other effects must also contribute to the stability of the (*E*)-isomer relative to that of the (*Z*) one. Indeed, the planarity of the first isomer implies that two stabilizing interactions take place between the oxygen atoms 4 and 8 and the two hydrogen atoms connected to carbon atoms 5 and 6. The distance between the two interacting atoms is about 2.61 Å, being somewhat less than the sum of the corresponding van der Waals radii of oxygen and hydrogen (1.5 Å and 1.2 Å respectively[21]). This fact suggests the occurrence of intramolecular C–H ··· O interactions, which must be responsible for most of the excess stability of the (*E*)-isomer relative to the (*Z*)-isomer. The remaining stability gain of this isomer can thus be attributed to the more effective electron delocalization allowed by the planarity of this isomer.

These conclusions are corroborated by calculations we carried out for the pair of (*E*)- and (*Z*)-glyoxal, OHC–CHO, conformers using the same level of theory. In this case, B3LYP/6-311G** calculations indicate that both isomers are planar, thus implying that the electronic delocalization effects have similar weight, and that the (*E*)-isomer is the most stable one by about 18.3 kJ mol$^{-1}$. The distance between the oxygen and the hydrogen atoms involved in the intramolecular C–H ··· O interaction is in this case 2.62 Å, very close to the corresponding distance observed in the fumarate/maleate isomers. Thus we may conjecture that most of the stability of dimethyl fumarate relative to dimethyl maleate results from H ··· O intramolecular interactions while a relatively smaller stabilization results from the effects of the electronic delocalization. Indeed, we had earlier noted with some surprise[22] that glyoxal and 1,3-butadiene had comparable stabilities as defined by the nearly identical reaction enthalpies

$$2CH_2X \longrightarrow XHC\text{–}CHX + H_2 \qquad (4)$$

for X = O and $CH_2$. We now wonder how much glyoxal is stabilized by such H ··· O intramolecular interactions.

**Calculated enthalpies of formation.** The relative stabilities of the two isomers were assessed by considering the energy variation of the following bond separation reaction,

$$CH_3O_2CCH{=}CHCO_2CH_3 + 2CH_4 \longrightarrow C_2H_4 + 2CH_3CO_2CH_3 \qquad (5)$$

**Table 7** Calculated electronic (hartree) and zero-point vibrational energies (kJ mol$^{-1}$) of the isomers

| Compound | $E_{\text{B3LYP/6-31G*}}$ | $E_{\text{B3LYP/6-311G**}}$ | $E_{\text{B3LYP/cc-pVTZ}}$ | $E_{\text{ZP/B3LYP/6-31G*}}$ | $E_{\text{total/B3LYP/6-31G*}}$[a] |
|---|---|---|---|---|---|
| DMeF | −534.345866 | −534.502579 | −534.558864 | 365.74 | 394.80 |
| DMeM | −534.333677 | −534.490681 | −534.547585 | 365.13 | 394.26 |

[a] $E_{\text{total}}$ ($T = 298.15$ K) $= E_{\text{trans}} + E_{\text{rot}} + E_{\text{ZP}} + \Delta_{0\,\text{K}}^{298.15\,\text{K}} E_{\text{vib}}$

**Table 8** Calculated reaction energies at $T = 0$ K and enthalpies at $T = 298.15$ K of the isomers

| | $\Delta_rE_T$/kJ mol$^{-1}$ at $T = 0$ K | | | $\Delta_rH°_T$/kJ mol$^{-1}$ at $T = 298.15$ K | | | |
|---|---|---|---|---|---|---|---|
| Compound | B3LYP/6-31G* | B3LYP/6-311G** | B3LYP/cc-pVTZ | B3LYP/6-31G* | B3LYP/6-311G** | B3LYP/cc-pVTZ | Exp. |
| DMeF | 47.8 | 40.5 | 35.1 | 49.4 | 42.1 | 36.7 | (27.3 ± 3.1) |
| DMeM | 15.8 | 9.2 | 5.5 | 17.9 | 11.4 | 7.6 | −(3.5 ± 3.1) |

**Table 9** Theoretical estimates of the standard enthalpies of formation in the gas phase at $T = 298.15$ K

| | $\Delta_fH_m°$(g)/kJ mol$^{-1}$ | | | |
|---|---|---|---|---|
| | B3LYP/6-31G* | B3LYP/6-311G** | B3LYP/cc-pVTZ | Exp. |
| Reaction 5 (DMeF) | −674.7 | −667.4 | −662.0 | −(652.6 ± 2.6) |
| Reaction 5 (DMeM) | −643.2 | −636.7 | −632.9 | −(621.8 ± 2.6) |
| Reaction 6 (DMeM) | −632.2 | −635.0 | −637.2 | −(621.8 ± 2.6) |

Because this reaction is isodesmic (the number of bonds of any formal type is conserved on each side of the equation), it is likely that the correlation and basis set deficiency errors will cancel, thus leading to reliable estimates of the enthalpies of formation of the isomers. The energies of all the other molecules in the reaction were obtained using the same calculation procedure as that described for the dimethyl fumarate and dimethyl maleate isomers. The reaction energies calculated at $T = 0$ K are presented in Table 8. The dimethyl fumarate isomer is predicted to be the most stable (by about 32 kJ mol$^{-1}$) isomer.

To compare the theoretical and experimental results the reaction enthalpies were calculated from the individual molecular energies by adding the zero-point vibrational energies and the thermal corrections from $T = 0$ K to $T = 298.15$ K. The reaction enthalpies at $T = 298.15$ K for the two isomers are also presented in Table 8, together with the experimental reaction enthalpy values derived from the experimental standard enthalpies of formation of all the compounds involved in the reactions at $T = 298.15$ K (the experimental standard enthalpies of formation of the auxiliary molecules were taken from reference 3).

One more isodesmic reaction is now suggested, *i.e.* that relating dimethyl maleate and dimethyl phthalate

$$o\text{-}C_6H_4(CO_2CH_3)_2 + C_2H_4 \longrightarrow CH_3O_2CCH{=}CHCO_2CH_3 + C_6H_6 \quad (6)$$

The theoretical calculations describe correctly the thermochemical stability that is observed experimentally. Table 9 shows the theoretical estimates of the standard enthalpies of formation in the gas phase obtained from the isodesmic reactions. The experimental values of $\Delta_fH_m°$ (g) are presented for comparison in the last column of the same table (the experimental standard enthalpy of formation of benzene is from reference 3, that of dimethyl phthalate from reference 23).

## Conclusions

Through a judicious combination of experimental thermochemical determinations and high-level theoretical calculations, we have determined the standard enthalpies of formation of the isomeric dimethyl fumarate and dimethyl maleate esters in the gas phase. It is found that the former species, the (*E*)-isomer, is more stable than the latter by some 30 kJ mol$^{-1}$. While perhaps, we are not surprised by this difference and the fact that the fumarate isomer is the more stable, we are nonetheless pleased.

## Experimental

### Materials

Dimethyl fumarate (DMeF) and dimethyl maleate (DMeM) are both commercial products (Aldrich Chemical Co.). The dimethyl fumarate [624–49–7] was used without additional purification whilst the dimethyl maleate [624–48–6] was purified by vacuum distillation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratios, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of the sample were: DMeF (0.9993 ± 0.0002) and DMeM (0.9963 ± 0.0004). The crystalline dimethyl fumarate was studied by differential scanning calorimetry (DSC) over the temperature range $T = 298$ K to its temperature of fusion (375.28 ± 0.08 K), and no impurities were found. Measurements were performed with a Setaram DSC 141 apparatus at a heating rate of $1.67 \times 10^{-2}$ K s$^{-1}$. The purity of the liquid dimethyl maleate was also assessed by GLC..

The density of DMeF was estimated to be $\rho = 1.0$ g cm$^{-3}$ and the density of DMeM was taken as $\rho = 1.152$ g cm$^{-3}$.[24]

### Combustion calorimetry

The combustion experiments were performed with a static bomb calorimeter. The apparatus and technique have been described elsewhere.[25,26] Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190 p) was used for calibration of the bomb. Its massic energy of combustion is $-\Delta_cu = (26432.3 \pm 3.8)$ J g$^{-1}$ under certified conditions ($p = 3$ MPa). The calibration results were corrected to give the energy equivalent $\varepsilon_{cal}$ corresponding to the average mass of water added to the calorimeter, 3119.6 g. From six calibration experiments that were performed $\varepsilon_{cal} = (16004.8 \pm 1.6)$ J K$^{-1}$, where the uncertainty quoted is the standard deviation of the mean. Sealed melinex bags were used in the combustion of the liquid compound using the technique described by Skinner and Snelson,[27] who determined the specific energy of combustion of dry melinex to be $-\Delta_cu° = (22902 \pm 5)$ J g$^{-1}$. This value was confirmed in our laboratory.

### Calvet microcalorimetry

The enthalpies of sublimation and of vaporization were measured using the "*vacuum sublimation*" drop microcalorimetric method,[28] which, in the case of vaporization, was previously tested in the Porto laboratory.[29] Samples, about 3–4 mg of the solid compound and 8–10 mg of the liquid, in thin glass capillary tubes sealed at one end at room temperature were dropped into the hot reaction vessel of a high temperature Calvet microcalorimeter held at a convenient temperature *T*, and were then removed from the hot zone by *vacuum evaporation*. The observed enthalpies of evaporation were corrected to $T = 298.15$ K by using the value of $\Delta_{298.15\,\mathrm{K}}^{T}H_m°$ (g) estimated by a group method using values of Stull *et al.*[30] The microcalorimeter was calibrated *in situ* for these measurements by using the reported enthalpies of sublimation of naphthalene[30] and of vaporization of undecane.[3]

### Computational details

The most stable conformations of the isomeric dimethyl fumarate and dimethyl maleate were obtained using density functional theory (DFT) with the Becke 3-parameter hybrid exchange[31] and Lee–Yang–Parr[32] correlation density functional (B3LYP) and three different basis sets: 6-31G*,[33,34] 6-311G**[35,36] and cc-pVTZ.[37] The harmonic vibrational frequencies were obtained at the optimum B3LYP/6-31G* geometries, using the same basis set and were scaled by a factor of 0.9614[38] in order to correct for anharmonicity. All calculations were performed using the UK version of GAMESS.[39,40]

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## References

1 *The Chemistry of Functional Groups Supplement A3: The Chemistry of Doubly-Bonded Functional Groups*, ed. S. Patai, Wiley, Chichester, 1997 .The importance of the >C=C< functional group is recognized immediately when it is recalled that it was this functionality, the all-hydrocarbon olefins, that launched the "Patai" series of monographs, *The Chemistry of Alkenes*, ed. S. Patai, Interscience, New York, 1964.

2 For a review of the thermochemistry of hydrocarbons containing the >C=C< functional group (*i.e.*, one in which hetero atoms or non-carbon substituents are discussed) see, S. W. Slayden and J. F. Liebman, in *The Chemistry of Functional Groups Supplement A3: The Chemistry of Doubly-Bonded Functional Groups*, ed. S. Patai, Wiley, Chichester, 1997, p. 537.

3 All unreferenced enthalpies of formation in this paper come from the archival source, J. B. Pedley, in *Thermochemical Data and Structures of Organic Compounds*, TRC Data Series, College Station, Texas, 1994, Vol. I.

4 R. B. Turner, D. E. Nettleton Jr. and M. Perelman, *J. Am. Chem. Soc.*, 1958, **80**, 1430; J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, 1961, **65**, 267; W. von E. Doering, W. R. Roth, F. Bauer, R. Breuckmann, T. Ebbrecht, M. Herbold, R. Schmidt, H. W. Lennartz, D. Lenoir and R. Boese, *Chem. Ber.*, 1989, **122**, 1263.

5 R. B. Turner, A. D. Jarrett, P. Goebel and B. J. Mallon, *J. Am. Chem. Soc.*, 1973, **95**, 790.

6 X = $OCH_3$: J. T. Waldron and W. H. Snyder, *J. Am. Chem. Soc.*, 1973, **95**, 5491. X = F: N. C. Craig and E. A. Entemann, *J. Am. Chem. Soc.*, 1961, **83**, 3047.

7 S. Furuyama, D. M. Golden and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 3204.

8 W. Fang and D. W. Rogers, *J. Org. Chem.*, 1992, **57**, 2294.

9 W. R. Roth, O. Adamczak, R. Breuckmann, H. W. Lennartz and R. Boese, *Chem. Ber.*, 1991, **124**, 2499.

10 G. Pilcher, in *The Chemistry of Functional Groups Supplement B: The Chemistry of Acid Derivatives*, ed. S. Patai, Wiley, Chichester, 1992, p. 51.

11 W. N. Hubbard, D. W. Scott, G. Waddington, in *Experimental Thermochemistry: Standard States and Corrections for Combustions in a Bomb at Constant Volume*, ed. F. D. Rossini, Interscience, New York, 1956, Vol. 1, Ch. 5.

12 J. Coops, R. S. Jessup, K. Van Nes, in *Experimental Thermochemistry: Calibration of Calorimeters for Reactions in a Bomb at Constant Volume*, ed. F. D. Rossini, Interscience, New York, 1956, Vol. 1, Ch. 3.

13 The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, 1982, **11**, Suppl. 2.

14 F. D. Rossini, in *Experimental Thermochemistry: Assignment of Uncertainties to Thermochemical Data*, ed. F. D. Rossini, Interscience, New York, 1956, Vol. 1, Ch. 14, p. 297.

15 CODATA, *J. Chem. Thermodyn.*, 1978, **10**, 903.

16 J. S. Chickos, W. E. Acree Jr. and J. F. Liebman, *J. Phys. Chem. Ref. Data*, 1999, **28**, 1535.

17 A. Wassermann, *Z. Physik. Chem.*, 1930, **A146**, 418.

18 R. M. Stephenson and S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds*, Elsevier, New York, 1987.

19 K. K. Irikura, in *Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics*, ed. K. K. Irikura and D. J. Frurip, ACS Symposium Series 677, American Chemical Society, Washington DC, 1998.

20 R. W. F. Bader, M. Carroll, J. R. Cheeseman and C. Chang, *J. Am. Chem. Soc.*, 1987, **109**, 7968; R. W. F. Bader, T. S. Slee, D. Kremer and E. Kraka, *J. Am. Chem. Soc.*, 1983, **105**, 5061.

21 See, for example, J. E. Huheey, E. A. Keiter and R. L. Keiter, in *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edn., Harper Collins College Publishers, New York, 1993.

22 J. F. Liebman, *Struct. Chem.*, 1992, **3**, 449.

23 M. V. Roux, P. Jiménez, J. Z. Dávalos, C. Turrión, H. Y. Afeefy and J. F. Liebman, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 887.

24 *Handbook of Chemistry and Physics*, 70th edn., ed. R. C. Weast, CRC Press Inc., Cleveland, Ohio, 1989–1990.

25 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *Rev. Port. Quím.*, 1984, **26**, 163.

26 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *J. Chem. Thermodyn.*, 1984, **16**, 1149.

27 H. A. Skinner and A. Snelson, *Trans. Faraday Soc.*, 1960, **56**, 1776.

28 F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. L. Leung, I. M. Paz-Andrade and H. A. Skinner, *J. Organomet. Chem.*, 1975, **97**, 221.

29 M. A. V. Ribeiro da Silva, M. A. R. Matos and L. M. P. F. Amaral, *J. Chem. Thermodyn.*, 1995, **27**, 565.

30 D. R. Stull, E. F. Westrum, G. C. Sinke, in *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.

31 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

32 C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev.*, 1998, **37**, 785.

33 P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **66**, 217.

34 M. M. Francl, W. J. Pietro, J. W. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

35 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

36 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

37 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **98**, 1358.

38 P. A. Scott and L. Radom, *J. Chem. Phys.*, 1996, **100**, 16502.

39 UK-GAMESS is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, and P. Sherwood, with contributions from R. D. Amos, R. J. Buenker, H. J. J. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R. J. Harrison, A. P. Rendell, V. R. Saunders, A. J. Stone and A. H. de Vries. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendoloski, NRCC Software Catalog, **Vol. 1**, Program No. QG01, GAMESS, 1980.

40 The DFT module within GAMESS-UK was developed by Dr P. Young under the auspices of the EPSRC's Collaborative Computational Project No. 1 (CCP1) (1995–1997).