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Calorimetric and Computational Thermochemical Study of 3,3-Tetramethyleneglutaric Acid, 3,3-Tetramethyleneglutaric Anhydride, and 3,3-Tetramethyleneglutarimide

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The standard ($p° = 0.1$ MPa) molar energies of combustion in oxygen, at $T = 298.15$ K, of solid 3,3-tetramethyleneglutaric acid and the related 3,3-tetramethyleneglutaric anhydride and 3,3-tetramethyleneglutarimide were measured by static bomb combustion calorimetry. The values of the standard molar enthalpies of sublimation, at $T = 298.15$ K, were obtained by Calvet microcalorimetry, allowing the calculation of the standard molar enthalpies of formation of the compounds, in the gaseous state, at $T = 298.15$ K. The geometries of the experimentally studied compounds were fully optimized using density functional theory with the B3LYP functional and extended basis sets. More accurate energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the cc-pVTZ basis set. From these calculations the standard molar enthalpies of formation of 3,3-tetramethyleneglutaric acid, 3,3-tetramethyleneglutaric anhydride, and 3,3-tetramethyleneglutarimide were estimated using isodesmic reactions involving glutaric acid, glutaric anhydride, and glutarimide, respectively. Experimental and computational results were used in the discussion of the interrelation of energetics and structure in these compounds and compared with other structurally related compounds.

Introduction

3,3-Tetramethyleneglutaric acid (cyclopentane-1,1-diacetic acid), among other structurally diverse compounds such as some derivatives of benzoxazine, coumarin, flavone, naphthalene, phthalazine, quinazoline, quinoline, rhodanine and xanthone, has been found to be an inhibitor of the enzyme aldose reductase, crucial in the treatment of diabetic complications such as cataract formation.[1]

The Zn salt of 3,3-tetramethyleneglutaric acid "fixes" CO_2 to form copolymers[2] by reaction with propylene oxide, while a novel copolymer may be formed from the reaction of ethylene sulfite with 3,3-tetramethyleneglutaric anhydride.[3] A highly studied pharmaceutical buspirone (or more properly the *N*-(2-pyrimidinyl-piperazinyl-*N′*-tetramethylene) derivative of 3,3-tetramethyleneglutarimide) has been employed for treatment of depression and of Huntington's disease.[4]

We have previously studied the thermochemistry of other carboxylic acids, their anhydrides, and their imides such as those of maleic acid,[5] phthalic acid,[5] isatoic acid,[6] diphenic acid,[7] benzene-1,2,4,5-tetracarboxylic acid,[8] 2-sulfobenzoic acid,[9] and related species. In that glutaric acid and the related one-ring species, glutaric anhydride and imide, have been studied,[10] we have now proceeded to the experimental and computational study of 3,3-tetramethyleneglutaric acid (cyclopentane-1,1-diacetic acid, here abbreviated 3,3-tmg acid), 3,3-tetramethyleneglutaric anhydride (8-oxaspiro[4.5]decane-7,9-dione, spiro[tetrahydropyran [4,1′]cyclopentane]-2,6-dione, likewise 3,3-tmg anhydride), and 3,3-tetramethyleneglutarimide (8-azaspiro[4.5]decane-7,9-dione, spiro[piperidine[4,1′]cyclopentane]-2,6-dione, likewise 3,3-tmg imide). We additionally note that these are spiro compounds containing heterocyclic rings, and as such surprises may be expected for this class of such multi-ring species,[10−12] relatively understudied at least by thermochemists interested in enthalpies of formation.

The standard molar energies of combustion in oxygen, at $T = 298.15$ K, of the solid compounds were measured by static bomb combustion calorimetry. The values of the standard molar enthalpies of sublimation, at $T = 298.15$ K, were obtained by Calvet microcalorimetry, allowing the calculation of the standard molar enthalpies of formation, in the gaseous phase, at $T = 298.15$ K.

The geometries of the studied compounds were fully optimized using density functional theory (DFT) with the B3LYP functional and extended basis sets. More accurate energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the cc-pVTZ basis set. From these calculations the standard molar enthalpies of formation of 3,3-tetramethyleneglutaric acid, 3,3-tetramethyleneglutaric anhydride, and 3,3-tetramethyleneglutarimide were estimated using isodesmic reactions involving glutaric acid, glutaric anhydride, and glutarimide, respectively.

Experimental and computational results were used in the discussion of the interrelation of energetics and structure in these compounds and compared with other structurally related compounds.

Experimental Section

Materials. 3,3-Tetramethyleneglutaric acid and its respective dianhydride were obtained commercially from Aldrich with the assigned mass fraction purities of 99.7% 3,3-tetramethylene-

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glutaric acid [16713-66-9] and 99.8% 3,3-tetramethyleneglutaric anhydride [5662-95-3]. 3,3-Tetramethyleneglutarimide [1075-89-4] was obtained from Acros Organics with the assigned mass fraction purity of more than 99%. The compounds were further purified by repeated sublimation under reduced pressure before the calorimetric experiments.

The final purity of the compounds was assessed by differential scanning calorimetric (DSC) analysis using the fractional fusion technique.[13] The DSC experiments were performed with a Setaram DSC 141 calorimeter. The samples were hermetically sealed in stainless steel crucibles, and the heating rate was 1.67×10^{-2} K s^{-1}. The power scale of the calorimeter was calibrated with high-purity indium (mass fraction > 0.99999), and its temperature scale was calibrated by measuring the melting temperature of the following three high-purity reference materials:[14] naphthalene, benzoic acid, and indium. No phase transitions were observed between the temperature of 298.15 K and the melting temperature of the compound.

The compositional purity of the crystalline samples was also assessed via carbon dioxide recovery ratios. 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 sample were 1.0002 ± 0.0003 for 3,3-tetramethyleneglutaric acid, 0.9998 ± 0.0003 for 3,3-tetramethyleneglutaric anhydride, and 1.0001 ± 0.0001 for 3,3-tetramethyleneglutarimide.

The specific densities of the samples were estimated from the mass and volume of the samples and were taken as $\rho = 0.93$ g cm^{-3} (3,3-tetramethyleneglutaric acid), $\rho = 1.14$ g cm^{-3} (3,3-tetramethyleneglutaric anhydride), and $\rho = 1.00$ g cm^{-3} (3,3-tetramethyleneglutarimide).

Combustion Calorimetry. The energies of combustion of the compounds were measured using a static bomb calorimeter. Since the apparatus and the technique have been described previously,[15,16] only a brief description will be given here. The energy equivalent of the calorimeter was determined from the combustion of benzoic acid, BDH Thermochemical Standard, batch 69376/01, certified at Manchester University, having a massic energy of combustion of $\Delta_c u = -(26\,435.1 \pm 3.5)$ J g^{-1}, under certificate conditions. Calibration experiments were carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 cm^3 of water added to the bomb. One set of seven calibration experiments was performed leading to the value of the energy equivalent of the calorimeter: $\varepsilon_{\mathrm{cal}} = 16\,005.0 \pm 2.0$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

For all experiments, the samples in the pellet form were ignited at $T = 298.150 \pm 0.001$ K in oxygen, at a pressure of 3.04 MPa. A volume of water of 1.00 cm^3 was added to the bottom of the bomb where only water vapor is in brief contact with the compound, minimizing any possibility of any ring opening or hydrolysis of the anhydride or imide.

The electrical energy for ignition ΔU(ign) was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse of empirical formula $CH_{1.686}O_{0.843}$, the specific energy of combustion is $\Delta_c u^\circ = -16\,240$ J g^{-1},[17] a value previously confirmed in our laboratory. The corrections for nitric acid formation $\Delta U(HNO_3)$ were based on -59.7 kJ mol^{-1},[18] for the molar energy of formation of 0.1 mol dm^{-3} HNO_3(aq) from N_2(g), O_2(g), and H_2O(l). The crystalline compounds were burnt in pellet form. The mass of compound, *m*(compound), used in each experiment was determined from the total mass of carbon dioxide, *m*(CO_2,total), produced after allowing for that formed from the cotton thread fuse and Melinex in the case of 3,3-tetramethyleneglutarimide. The pellets of this compound were enclosed in polyester bags made of Melinex, using the technique described by Skinner and Snelson,[19] who determined the specific energy of combustion of dry Melinex as $\Delta_c u^\circ = -(22902 \pm 5)$ J g^{-1}. This value was confirmed in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032), and the mass of carbon dioxide produced from it was calculated using the factor previously reported.[19]

For each compound, the Washburn corrections to the standard state to calculate the standard massic energy of combustion, $\Delta_c u^\circ$, were made by the procedure given by Hubbard et al.[20] An estimated pressure coefficient of specific energy $(\partial u/\partial p)_T = -0.2$ J g^{-1} MPa^{-1} at $T = 298.15$ K, a typical value for most solid organic compounds, was assumed.[21]

Calvet Microcalorimetry. The standard molar enthalpies of sublimation were measured using the "vacuum sublimation" drop microcalorimetric method.[22] Samples, about 3−5 mg of the crystalline compounds contained in thin glass capillary tubes sealed at one end, were dropped from room temperature into the hot reaction vessel in the Calvet high-temperature microcalorimeter (SETARAM HT 1000D) held at a convenient temperature *T* and then removed from the hot zone by vacuum sublimation. Simultaneously, an empty capillary tube was dropped into the reference calorimetric cell. For these measurements, the microcalorimeter was calibrated in situ using the reported standard molar enthalpy of sublimation of naphthalene, 72.600 ± 0.600 kJ mol^{-1}.[23] Accuracy tests were performed in each case. The observed enthalpies of sublimation $\Delta_{\mathrm{cr},298.15\,\mathrm{K}}^{\mathrm{g},T}H_{\mathrm{m}}^{\circ}$ were corrected to $T = 298.15$ K using the equation

$$\Delta_{298.15\,\mathrm{K}}^{T}H_{\mathrm{m}}^{\circ}(g) = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}^{\circ}(g)\,\mathrm{d}T \qquad (1)$$

where *T* is the temperature of the hot reaction vessel and $C_{p,\mathrm{m}}^{\circ}(g)$ is the molar heat capacity of gaseous of the compounds. The heat capacity and its temperature dependence for gaseous 3,3-tetramethyleneglutaric acid, 3,3-tetramethyleneglutaric anhydride, and 3,3-tetramethyleneglutarimide, respectively

$$C_{p,\mathrm{m}}^{\circ}(g)/(\mathrm{J\ mol^{-1}\ K^{-1}}) = -0.000398(T/\mathrm{K})^2 + 0.8996(T/\mathrm{K}) - 31.625 \qquad (2)$$

$$C_{p,\mathrm{m}}^{\circ}(g)/(\mathrm{J\ mol^{-1}\ K^{-1}}) = -0.000310(T/\mathrm{K})^2 + 0.7821(T/\mathrm{K}) - 36.277 \qquad (3)$$

$$C_{p,\mathrm{m}}^{\circ}(g)/(\mathrm{J\ mol^{-1}\ K^{-1}}) = -0.000361(T/\mathrm{K})^2 + 0.857(T/\mathrm{K}) - 44.043 \qquad (4)$$

were derived from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP density functional and the 6-31G* basis set. The atomic weights of the elements were those recommended by the IUPAC commission.[24]

Computational Details. The geometries of the studied compounds were fully optimized using DFT with the Becke three-parameter hybrid exchange[25] and Lee−Yang−Parr[26] correlation density functional (B3LYP) and two basis sets: 6-31G*[27] and 6-311G**.[28] Harmonic vibrational frequencies were calculated through construction and diagonalization of the Hessian matrices at the optimum B3LYP/6-31G* molecular geometries obtained using the same basis set. This procedure allowed characterizing these equilibrium geometries as true minima and obtaining the corrections needed to derive energies at the temperature of 298.15 K. More accurate energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the triple-ζ correlation

TABLE 1: Summary of DSC Results

compound	T_{fus}/K	$\Delta_{cr}^{l}H_m^\circ(T_{fus})$/ kJ mol^{-1}	purity/mol %
3,3-tmg acid	452.90 ± 0.09	32.14 ± 0.42	99.88 ± 0.02
3,3-tmg anhydride	338.44 ± 0.04	15.27 ± 0.17	99.89 ± 0.03
3,3-tmg imide	426.56 ± 0.20	24.17 ± 0.68	99.82 ± 0.02

TABLE 2: Typical Combustion Experiments at T = 298.15 K[a]

	3,3-tmg acid	3,3-tmg anhydride	3,3-tmg imide
$m(CO_2$,total)/g	1.570 71	1.644 41	1.766 86
m(compound)/g	0.735 62	0.696 60	0.689 45
m(fuse)/g	0.003 67	0.002 44	0.002 66
m(Melinex)/g	–	–	0.05649
ΔT_{ad}/K	1.124 32	1.188 79	1.334 76
ε_f/(J K^{-1})	16.75	16.55	16.28
$\Delta m(H_2O)$/g	−0.1	0.0	−0.2
$-\Delta U$(IBP)/J	18 012.44	19 045.36	21 382.56
ΔU(fuse)/J	59.60	39.57	43.20
ΔU(Melinex)/J	–	–	1293.70
ΔU(ign)/J	0.66	0.90	0.89
ΔU(carbon)/J	0.00	0.00	0.00
$\Delta U(HNO_3)$/J	1.16	0.60	34.15
ΔU_Σ/J	10.68	11.21	12.74
$-\Delta_c u^\circ$/(J g^{-1})	24 388.95	27 266.70	29 006.84

[a] $m(CO_2$,total) is the total mass of CO_2 formed in the experiment; m(compound) is the mass of compound burnt in the experiment; m(fuse) is the mass of fuse (cotton) used in the experiment; m(Melinex) is the mass of Melinex used in the experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of contents in the final state; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; ΔU(IBP) includes the ignition energy, ΔU(ign); ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(Melinex) is the energy of combustion of Melinex; ΔU(carbon) is the energy correction for carbon formation; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU_Σ is the energy correction to the standard state; $\Delta_c u^\circ$ is the standard massic energy of combustion.

TABLE 3: Individual Values of the Massic Energy of Combustion, at T = 298.15 K

3,3-tmg acid	3,3-tmg anhydride	3,3-tmg imide
	$-\Delta_c u^\circ$/(J g^{-1})	
24 379.93	27 266.70	29 031.72
24 358.88	27 261.17	29 006.84
24 348.22	27 264.20	29 019.21
24 407.22	27 277.86	29 029.78
24 424.81	27 272.42	29 015.68
24 389.68	27 261.21	29 013.35
24 385.87	27 233.65	29 006.16
24 388.95	27 248.06	
	$-\langle\Delta_c u^\circ\rangle$ (J g^{-1})	
24 385.4± 8.6	27 260.7 ± 4.9	29 017.5 ± 3.8

TABLE 4: Derived Standard (p° = 0.1 MPa) Molar Values in the Crystalline Phase, at T = 298.15 K (kJ mol^{-1})

compound	$\Delta_c U_m^\circ$(cr)	$\Delta_c H_m^\circ$(cr)	$\Delta_f H_m^\circ$(cr)
3,3-tmg acid	−4540.7 ± 3.4	−4544.4 ± 3.4	−998.0 ± 3.6
3,3-tmg anhydride	−4585.0 ± 2.1	−4588.7 ± 2.1	−667.9 ± 2.4
3,3-tmg imide	−4851.9 ± 2.1	−4856.2 ± 2.1	−543.3 ± 2.4

TABLE 5: Standard (p° = 0.1 MPa) Molar Enthalpies of Sublimation, at T = 298.15 K

compound	no. expts	T/K	$\Delta_{cr,298.15\,K}^{g,T}H_m^\circ$/ kJ mol^{-1}	$\Delta_{298.15\,K}^{T}H_m^\circ$(g)/ kJ mol^{-1}	$\Delta_{cr}^{g}H_m^\circ$ (298.15 K)/ kJ mol^{-1}
3,3-tmg acid	8	436	160.6 ± 2.4	33.7	126.9 ± 2.4
3,3-tmg anhydride	6	375	111.1 ± 1.1	14.7	96.4 ± 1.1
3,3-tmg imide	6	412	131.2 ± 2.0	24.4	106.8 ± 2.0

TABLE 6: Derived Standard (p° = 0.1 MPa) Molar Values of the Enthalpies of Formation in the Gas Phase, at T = 298.15 K (kJ mol^{-1})

compound	$\Delta_f H_m^\circ$(cr)	$\Delta_{cr}^{g}H_m^\circ$	$\Delta_f H_m^\circ$(g)
3,3-tmg acid	−998.0 ± 3.6	126.9 ± 2.4	−871.1 ± 4.3
3,3-tmg anhydride	−667.9 ± 2.4	96.4 ± 1.1	−571.5 ± 2.6
3,3-tmg imide	−543.3 ± 2.4	106.8 ± 2.0	−436.5 ± 3.1

consistent basis set, cc-pVTZ.[29] All calculations were performed using the U.K. version of GAMESS.[30,31]

Results and Discussion

Experimental Results. The purity of the compounds was assessed using differential scanning calorimetry (DSC). The temperatures (observed at the onset of the calorimetric peaks) and enthalpies of fusion and the molar fractions of purity were computed from the DSC thermograms; the DSC results are summarized in Table 1. The uncertainties assigned to the results are twice the standard deviation of the mean of six independent runs.

Results for a typical combustion experiment of each compound are given in Table 2. The symbols in this table have the same meaning as in ref 20. As samples were ignited at T = 298.15 K

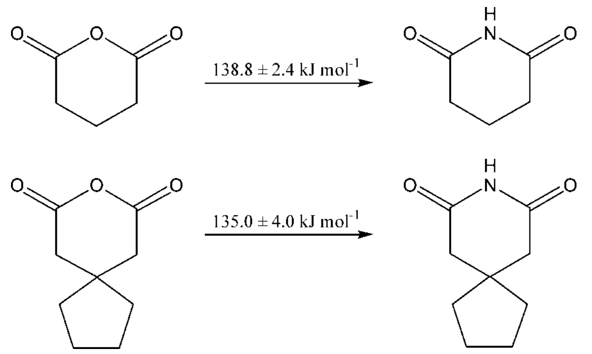
$$\Delta U(\mathrm{IBP}) = -\{\varepsilon_{cal} + c_p(\mathrm{H_2O,l})\,\Delta m(\mathrm{H_2O}) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\mathrm{ign}) \quad (5)$$

where ΔU(IBP) is the energy associated with the isothermal bomb process, $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, $c_p(H_2O$,l) is the specific heat capacity of liquid water, ε_f is the energy of the bomb contents after ignition, ΔT_{ad} is the adiabatic temperature raise, and ΔU(ign) is the energy of ignition. The individual results of the massic energy of combustion, $\Delta_c u^\circ$, at T = 298.15 K, of all combustion experiments, together with the mean value and its standard deviation, are given for each compound in Table 3. Table 4 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U_m^\circ$(cr) and $\Delta_c H_m^\circ$(cr), and the standard molar enthalpies of formation of the compounds in the crystalline phase $\Delta_f H_m^\circ$(cr) at T = 298.15 K. In accordance with customary thermochemical practice,[32] 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 and in the values of auxiliary quantities used. To derive $\Delta_f H_m^\circ$(cr) from $\Delta_c H_m^\circ$(cr), the standard molar enthalpies of formation of H_2O(l) and CO_2(g), at T = 298.15 K, were taken respectively as −(285.830 ± 0.042) kJ mol^{-1} [33] and −(393.51 ± 0.13) kJ mol^{-1}.[33]

The standard molar enthalpies of sublimation were measured by Calvet microcalorimetry. The experimental results are given in Table 5 with uncertainties of twice the standard deviation of the mean.

The standard molar enthalpies of formation in the gaseous state, at T = 298.15 K, are summarized in Table 6.

Considering the enthalpic increments from glutaric anhydride to glutarimide and 3,3-tetramethyleneglutaric anhydride to 3,3-tetramethyleneglutarimide,[10] we found that they are equal within the experimental uncertainties.



Consider the following scheme involving the three experimentally studied compounds 3,3-tetramethyleneglutaric acid, 3,3-tetramethyleneglutaric anhydride, and 3,3-tetramethyleneglutarimide. The enthalpic increments for the spiroannelation of the cyclopentane ring are equal within the experimental uncertainty for glutaric anhydride and glutarimide. The spiroannelation of the cyclopentane ring in glutaric acid results in an enthalpic increment of only -30.9 ± 4.6 kJ mol^{-1}. These data may additionally be compared with those for propane and 1,1-dimethylcyclopentane, i.e., the doubly decarboxylated analogues of glutaric acid and its tetramethylene counterpart, respectively. The difference is $(-138.2 \pm 1.0) - (-104.7 \pm 0.5) = -33.5 \pm 1.2$ kJ mol^{-1}. Other meaningful comparisons are between cyclopentane and spiro[4.4]nonane, and between cyclohexane and spiro[4.5]decane, all hydrocarbon counterparts of glutaric anhydride and imide, and their tetramethylene counterparts. For the smaller spiro compound we find the enthalpy of formation of the newly measured value[12] of -99.5 ± 1.2 kJ mol^{-1} and accordingly a difference with cyclopentane of $(-99.5 \pm 1.2) - (-76.4 \pm 0.7) = -23.1 \pm 1.4$ kJ mol^{-1}. For cyclohexane, the difference is $(-145.1 \pm 2.1) - (-123.3 \pm 0.8) = -21.8 \pm 2.2$ kJ mol^{-1}.[10] As will be described later, the glutaric anhydride and glutarimide fragments suffer only very small conformational changes when the corresponding tetramethylene molecules are formed: in fact, the groups $-$C(=O)$-$O$-$C(=O)$-$ and $-$C(=O)$-$NH$-$C(=O)$-$ remain absolutely planar. This contrasts with the other compounds mentioned for which much larger conformational changes occur. For instance, whereas tetramethyleneglutaric acid has an equilibrium conformation that allows for intramolecular hydrogen bond formation, glutaric acid adopts a less distorted, more extended conformation which forfeits this otherwise stabilizing interaction. This severe conformational change could then be responsible for the observed decrease of stabilization observed. We must, however, be careful in accepting such explanations, since the lack of knowledge of the thermochemistry of spiro compounds in general prevents this conclusion from being adequately supported or rejected. The enthalpy of formation changes accompanying introduction of a five-membered ring are as follows: for glutaric acid, the change is -30.9 ± 4.6 kJ mol^{-1}, while for its anhydride and imide the changes are -39.1 ± 3.2 and -42.9 ± 1.5 kJ mol^{-1} respectively; for the carbocyclic cyclopentane, the change is -23.1 ± 1.4 kJ, and for cyclohexane, it is -21.8 ± 2.2 kJ mol^{-1}. From where does this spread of values, ca. -22 to -43 kJ mol^{-1} arise?

It is clear that imides, anhydrides, and hydrocarbons have different responses to ring sizes, and therefore very plausibly to spiroannelation. The difference of the enthalpies of formation of gaseous succinimide and glutarimide is 18.2 ± 2.3 kJ mol^{-1}, that of succinic anhydride and glutaric anhydride is 4.5 ± 2.5 kJ mol^{-1}, and that of cyclopentane and cyclohexane is 46.9 ± 1.1 kJ mol^{-1}, respectively. As such, we accept the qualitative lack of understanding of the effects of tetramethylene or cyclopentyl rings into our diverse six-membered rings and acyclic pentane.

Theoretical Results. The geometries of the compounds have been fully optimized using the B3LYP density functional and the 6-31G* and 6-311G** basis sets. All molecules show nonplanar geometries. 3,3-Tetramethyleneglutaric acid presents a intramolecular hydrogen bond, O$-$H···O, between the O$-$H bond of one of the carboxyl groups and the C=O bond of the other carboxyl group. In the anhydride the atoms of the $-$C(=O)$-$O$-$C(=O)$-$ group are in the same plane, as are the atoms of the $-$C(=O)$-$NH$-$C(=O)$-$ group in the imide. A crystal structure study of 8-{4-[4-(pyrimidin-2-yl)-piperazin-1-yl]butyl}-8-azaspiro[4.5]decane-7,9-dione, generic name buspirone, also shows this planarity.[34] Single-point calculations were then performed with the consistent-correlation cc-pVTZ basis set, using the optimized B3LYP/6-311G** geometries. The resulting electronic energies are shown in Table 7 under the appropriate headings, as are the thermal corrections to $T = 298.15$ K. In this table we also show the corresponding energies of some auxiliary molecules.

The enthalpy of formation of the 3,3-tetramethyleneglutaric acid was estimated using the following isodesmic reactions:

3,3-tetramethyleneglutaric acid +
cyclobutane → 1,1-cyclobutanedicarboxylic acid +
1,1-dimethylcyclopentane (6)

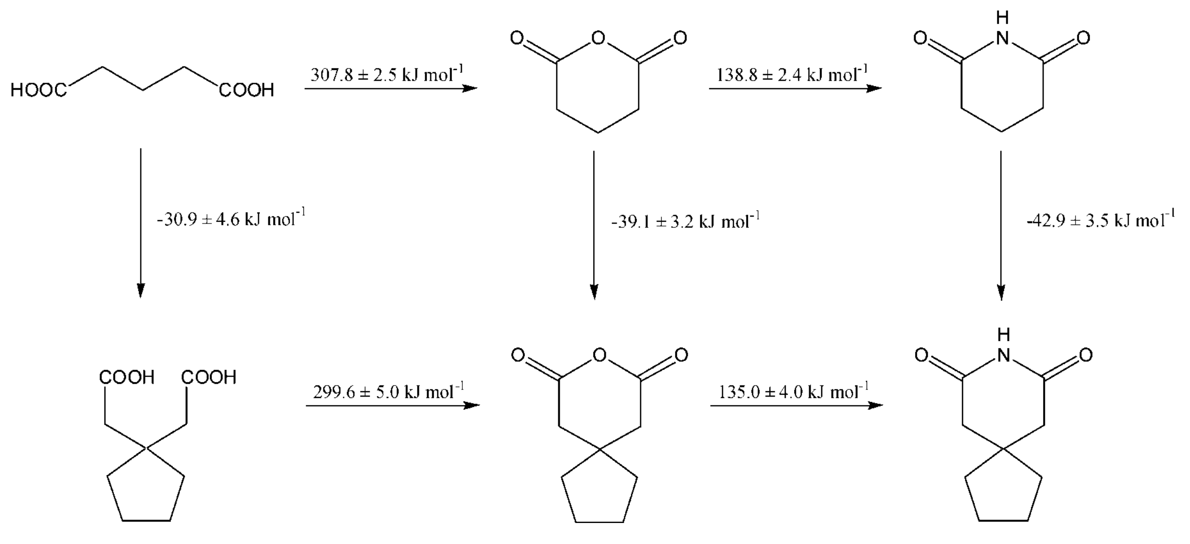


TABLE 7: B3LYP Calculated Electronic Energies (hartrees) and Thermal Corrections to $T = 298.15$ K (kJ mol^{-1})

compound	6-31G*	6-311G**	cc-pVTZ^a	$E_{\mathrm{total/6\text{-}31G^*}}$^{b}
cyclobutane	−157.213 150	−157.258 570	−157.274 102	303.26
1,1-cyclobutanedicarboxylic acid	−534.346 065	−534.512 760	−534.566 555	396.58
1,1-dimethylcyclopentane	−275.185 282	−275.263 570	−275.290 171	538.72
ethane	−79.830 413	−79.857 274	−79.865 587	206.64
glutaric acid	−496.275 198	−496.436 395	−496.487 895	379.11
glutaric anhydride	−419.833 105	−419.954 039	−419.997 822	303.14
glutarimide	−399.982 352	−400.099 874	−400.140 650	338.33
propane	−119.144 231	−119.182 194	−119.194 293	285.14
succinic acid	−456.962 172	−457.112 331	−457.160 077	300.50
succinic anhydride	−380.523 062	−380.633 312	−380.673 781	223.73
succinimide	−360.666 781	−360.773 747	−360.811 052	258.21
3,3-tetramethyleneglutaric acid	−652.316 631	−652.516 929	−652.581 044	636.18
3,3-tetramethyleneglutaric anhydride	−575.875 936	−576.037 503	−576.095 359	556.99
3,3-tetramethyleneglutarimide	−556.024 205	−556.182 385	−556.237 289	592.05
water	−76.408 955	−76.448 292	−76.461 256	63.01

[a] B3LYP/cc-pVTZ//B3LYP/6-311G**. [b] $E_{\mathrm{total}}(T = 298.15\ \mathrm{K}) = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{ZP}} + \Delta_{0\ \mathrm{K}}^{298.15\ \mathrm{K}} E_{\mathrm{vib}}$.

$$\text{3,3-tetramethyleneglutaric acid} + \text{glutaric anhydride} \rightarrow \text{3,3-tetramethyleneglutaric anhydride} + \text{glutaric acid} \quad (7)$$

$$\text{3,3-tetramethyleneglutaric acid} + \text{propane} \rightarrow \text{glutaric acid} + \text{1,1-dimethylcyclopentane} \quad (8)$$

$$\text{3,3-tetramethyleneglutaric acid} + \text{ethane} \rightarrow \text{succinic acid} + \text{1,1-dimethylcyclopentane} \quad (9)$$

The homologous reactions for the anhydride and imide are

$$\text{3,3-tetramethyleneglutaric anhydride} + \text{propane} \rightarrow \text{glutaric anhydride} + \text{1,1-dimethylcyclopentane} \quad (10)$$

$$\text{3,3-tetramethyleneglutaric anhydride} + \text{ethane} \rightarrow \text{succinic anhydride} + \text{1,1-dimethylcyclopentane} \quad (11)$$

$$\text{3,3-tetramethyleneglutarimide} + \text{propane} \rightarrow \text{glutarimide} + \text{1,1-dimethylcyclopentane} \quad (12)$$

$$\text{3,3-tetramethyleneglutarimide} + \text{ethane} \rightarrow \text{succinimide} + \text{1,1-dimethylcyclopentane} \quad (13)$$

$$\text{3,3-tetramethyleneglutarimide} + \text{glutaric anhydride} \rightarrow \text{3,3-tetramethyleneglutaric anhydride} + \text{glutarimide} \quad (14)$$

The computed enthalpies of formation are compared in Table 8 with the experimental values (the experimental standard molar enthalpies of formation of the auxiliary compounds were taken from ref 10). There is a difference of only about 1−13 kJ mol^{-1} between experimental and theoretical results.

We have also considered the dehydration reactions

$$\text{3,3-tetramethyleneglutaric acid} \rightarrow \text{3,3-tetramethyleneglutaric anhydride} + \text{water} \quad (15)$$

$$\text{glutaric acid} \rightarrow \text{glutaric anhydride} + \text{water} \quad (16)$$

$$\text{succinic acid} \rightarrow \text{succinic anhydride} + \text{water} \quad (17)$$

The reaction energies at $T = 0$ K and enthalpies at $T = 298.15$ K are presented in Table 9, together with the corresponding experimental results. There is good agreement between both sets of values.

TABLE 8: Estimated Enthalpies of Formation in the Gas Phase at $T = 298.15$ K by cc-pVTZ//6-311G^a**

	$\Delta_f H_m^\circ(g)$/ kJ mol^{-1}	Δ(expt − calcd)^b/ kJ mol^{-1}
(reaction *6*) 3,3-tetramethyleneglutaric acid	−882.2	11.1
(reaction *7*) 3,3-tetramethyleneglutaric acid	−864.6	−6.5
(reaction *8*) 3,3-tetramethyleneglutaric acid	−863.1	−8.0
(reaction *9*) 3,3-tetramethyleneglutaric acid	−858.6	−12.5
(reaction *10*) 3,3-tetramethyleneglutaric anhydride	−570.1	−1.4
(reaction *11*) 3,3-tetramethyleneglutaric anhydride	−573.3	1.8
(reaction *12*) 3,3-tetramethyleneglutarimide	−429.1	−7.4
(reaction *13*) 3,3-tetramethyleneglutarimide	−432.6	−3.9
(reaction *14*) 3,3-tetramethyleneglutarimide	−430.5	−6.0

[a] B3LYP/cc-pVTZ//B3LYP/6-311G**. [b] The experimental values of the enthalpies of formation of auxiliary molecules were taken from ref 10.

TABLE 9: Calculated Dehydration Reaction Energies at $T = 0$ K and Enthalpies at $T = 298.15$ K (kJ mol^{-1}) and Comparison with Experimental Results

	$\Delta_r E_{T=0\ \mathrm{K}}$	$\Delta_r H^\circ_{T=298.15\ \mathrm{K}}$	
	cc-pVTZ//6-311G** ^{a}	cc-pVTZ//6-311G** ^{a}	exptl^b
reaction *15*	64.2	50.5	57.8 ± 5.0
reaction *16*	75.7	65.2	66.0 ± 2.5
reaction *17*	65.8	54.5	47.5 ± 3.1

[a] B3LYP/cc-pVTZ//B3LYP/6-311G**. [b] The experimental values of the enthalpies of formation of auxiliary molecules were taken from ref 10.

Conclusions

A combined experimental and computational study has been carried out on the thermochemistry of 3,3-tetramethyleneglutaric acid, 3,3-tetramethyleneglutaric anhydride, and 3,3-tetramethyleneglutarimide. From the experimental side, standard molar enthalpies of combustion and enthalpies of sublimation for the three compounds led to the corresponding enthalpies of formation in the crystalline and gaseous phases. On the computational side estimates were obtained for the three compounds of the standard molar enthalpies of formation in the gas phase using a set of isodesmic reactions.

The comparison between the experimental and computational gas phase enthalpies of formation for the three compounds showed good agreement between these two procedures. The deviation between computed and experimental values is less than 13 kJ mol^{-1}.

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