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Thermochemical and Theoretical Studies on Cyclohexanediones

G. Pilcher,* O. G. Parchment, I. H. Hillier, F. Heatley, and D. Fletcher

Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

M. A. V. Ribeiro da Silva, M. L. C. C. H. Ferrão, M. J. S. Monte, and Fang Jiye

Departamento de Química, Faculdade de Ciências, Universidade do Porto, P4000 Porto, Portugal

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The following standard molar enthalpies of formation in the gaseous state at 298.15 K were determined from the enthalpies of combustion of the crystalline solids and the enthalpies of sublimation: 1,3-cyclohexanedione, -335.6 ± 1.6 kJ mol^{-1}; 1,4-cyclohexanedione, -332.6 ± 1.2 kJ mol^{-1}; 4,4-dimethyl-1,3-cyclohexanedione, -400.4 ± 2.7 kJ mol^{-1}; and 5,5-dimethyl-1,3-cyclohexanedione, -383.6 ± 1.9 kJ mol^{-1}. Ab initio calculations were made of the enthalpies of isomerization of the three cyclohexanediones and of the isomerization of 1,3-cyclohexanedione to its enol forms: the keto form of 1,3-cyclohexanedione in the gaseous state was predicted to be energetically more stable than the enol form by 18.0 kJ mol^{-1}. NMR spectra, however, showed the compound in the crystalline state to exist in the enol form with the molecules held together by intermolecular hydrogen bonds. The enthalpy of formation of 1,2-cyclohexanedione in the gaseous state, not amenable to experimental measurement, was predicted to be -300 ± 5 kJ mol^{-1}, and the conventional strain energies in the three cyclohexanedione isomers were estimated to be of similar magnitude, ca. 13 kJ mol^{-1}.

Introduction

Thermochemical measurements on diketones have been mainly concerned with β-diketone derivatives[1-3] which act as bidentate ligands to form coordination complexes with virtually every metal and metalloid in the periodic table. No measurements have been reported on the isomeric cyclohexanediones, of which 1,3-cyclohexanedione is of particular interest because of its potential for enolization. During crystallization, 1,3-cyclohexanedione assembles into either intermolecularly hydrogen-bonded chains or hexameric rings depending on the solvent conditions[4] and hence in the solid state exists in the enol form.

In this paper we report the standard molar enthalpies of combustion of the crystalline solids 1,3-cyclohexanedione, 1,4-cyclohexanedione, 4,4-dimethyl-1,3-cyclohexanedione, and 5,5-dimethyl-1,3-cyclohexanedione and their enthalpies of sublimation to derive the standard molar enthalpies of formation in the gaseous state. NMR studies were made on the two solid dimethyl-1,3-cyclohexanedione derivatives to determine their molecular structures. Ab initio calculations on the three cyclohexanedione isomers and on the enol forms of 1,3-cyclohexanedione were made to predict the enthalpies of isomerization of these species in the gaseous state. These calculations also permitted an indirect estimation of the enthalpy of formation of 1,2-cyclohexanedione as this compound was not amenable to measurement.

Experimental Section

Materials. 1,3-Cyclohexanedione (MC) and 1,4-cyclohexanedione (PC) (Aldrich) were crystallized repeatedly from an equimolar mixture of trichloromethane and diethyl ether and dried in vacuo. 4,4-Dimethyl-1,3-cyclohexanedione (4dmeMC) and 5,5-dimethyl-1,3-cyclohexanedione (5dmeMC) (Aldrich) were crystallized repeatedly from aqueous ethanol and dried over P_4O_{10}. Crystallizations were repeated until the recoveries of carbon dioxide from the combustion experiments were greater than 99.7%. Attempts to purify 1,2-cyclohexanedione by crystallization and by sublimation resulted in samples giving less than 97% carbon dioxide recoveries and so were unsuitable for experimental measurements. The average ratios of the masses of carbon dioxide observed to those calculated from the masses of the samples together with the densities of the samples were as follows: MC ($\rho = 1.086$ g cm^{-3}, 0.9981 ± 0.0003); PC ($\rho = 1.30$ g cm^{-3}, 0.9969 ± 0.0022); 4dmeMC ($\rho = 1.06$ g cm^{-3}, 0.9995 ± 0.0002); 5dmeMC ($\rho = 1.06$ g cm^{-3}, 0.9996 ± 0.0001). *n*-Hexadecane (Aldrich Gold Label), stored under nitrogen, for which from separate measurements $-\Delta_c u^0/\mathrm{J\ g^{-1}} = 47\,164.4 \pm 1.7$, was used as an auxiliary combustion aid for some of the measurements.

Combustion Calorimetry. The enthalpies of combustion of MC and PC were measured using the static-bomb calorimeter in Manchester[5] whereas 4dmeMC and 5dmeMC were measured using the static-bomb calorimeter in Porto.[6,7] The energy equivalents of the calorimeters were determined using the combustion of benzoic acid: in Manchester with N.B.S. SRM 39i for which under standard bomb conditions $-\Delta_c u/\mathrm{J\ g^{-1}} = 26\,434 \pm 3$, from 12 calibrations $\epsilon(\mathrm{calor}) = 15\,540.98 \pm 0.47$ J K^{-1} for an average mass of water added to the calorimeter of 2897.0 g; in Porto with Bureau of Analysed Samples CRM190p for which $-\Delta_c u/\mathrm{J\ g^{-1}} = 26\,431.8 \pm 3.7$, from 10 calibrations $\epsilon(\mathrm{calor}) = 16\,017.0 \pm 1.3$ J K^{-1} for an average mass of water added to the calorimeter of 3116.9 g.

The experimental conditions were similar for both calorimeters. Samples were ignited at 298.150 ± 0.001 K in oxygen at 3.04 MPa with 1 cm^3 of water added to the bomb. The electrical energy of ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^0 = 16\,250$ J g^{-1}.[8] Corrections for nitric acid formation were based on -59.7 kJ mol^{-1} for the molar energy of formation of 0.1 mol dm^{-3} $HNO_3(aq)$ from N_2, O_2, and $H_2O(l)$. Corrections for carbon formation were based on $\Delta_c u^0 = -33$ kJ g^{-1}.[8] The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that from the cotton thread fuse, hexadecane, and that lost due to carbon formation. For each compound at 298.15 K, $(\delta u/\delta p)_T$ was assumed to be -0.1 J g^{-1} MPa^{-1}, a value typical for most organic solids. For each compound, $\Delta_c u^0$ was calculated by the procedure given by Hubbard et al.[8] The relative atomic masses used were those recommended by the IUPAC Commission.[10]

Enthalpies of Sublimation. The enthalpies of sublimation of MC and PC were measured using the "vacuum-sublimation" drop

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TABLE I: Typical Combustion Measurements at 298.15 K (p^0 = 0.1 MPa)

	MC	PC	4dmeMC	5dmeMC
$m(CO_2,\text{total})/g$	2.50329	2.31975	2.20079	2.38369
$m(\text{cpd})/g$	1.06111	0.98339	0.48441	0.57005
$m(\text{hexadecane})/g$			0.31503	0.30457
$m(\text{fuse})/g$	0.00318	0.00240	0.00280	0.00301
$\Delta T_{ad}/K$	1.87783	1.74998	1.86982	2.00947
$\epsilon_f/J\ K^{-1}$	15.69	14.88	17.5	17.8
$\Delta m(H_2O)/g$	−2.6	−2.2	0.1	0.0
$-\Delta U(\text{IBP})/J$	29191.3	27205.5	29981.3	32220.5
$\Delta U(HNO_3)/J$	16.2	9.0	4.8	2.4
$\Delta U(\text{carbon})/J$	6.6	0.0	0.0	0.0
$\Delta U(\text{ignition})/J$	1.1	0.9	1.1	1.0
$\Delta U_\Sigma/J$	19.4	17.8	12.0	13.5
$-m\Delta_c u^0(\text{fuse})/J$	51.6	39.0	45.5	48.9
$-m\Delta_c u^0(\text{hexadecane})/J$			14858.2	14364.7
$-\Delta_c u^0(\text{cpd})/J\ g^{-1}$	27434.2	27598.1	31091.0	31209.5

TABLE II: Values of $-\Delta_c u^0$(J g^{-1}) at 298.15 K

MC	PC	4dmeMC	5dmeMC
27 440.6	27 597.8	31 091.0	31 211.3
27 425.1	27 598.1	31 103.4	31 198.2
27 448.8	27 591.0	31 078.7	31 220.5
27 438.9	27 589.0	31 088.9	31 213.5
27 438.0	27 594.1	31 099.9	31 197.6
27 434.2	27 604.3	31 098.6	31 209.5
		31 089.1	31 204.9
		31 081.9	31 204.3
		$-(\Delta_c u^0)/J\ g^{-1}$	
27 437.6 ± 3.2	27 595.7 ± 2.3	31 091.4 ± 3.1	31 207.5 ± 2.8

microcalorimetric method.[11] Samples, about 5 mg, of each compound contained in a thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in a Calvet microcalorimeter held at 380 K and then removed from the hot zone by vacuum sublimation. The observed enthalpies of sublimation, [H^0(g,380 K) − H^0_m(cr,298.15 K)] were corrected to 298.15 K using $\Delta^{380\ K}_{298.15\ K}H^0_m(g)$ estimated by a group method based on the values of Stull et al.[12] The microcalorimeter was calibrated in situ for these measurements using the reported enthalpy of sublimation of iodine.[13]

The enthalpies of sublimation of 4dmeMC and of 5dmeMC were derived from vapor pressures, measured using a Knudsen apparatus,[14] as functions of temperature. The apparatus permits the simultaneous operation of three Knudsen cells with different effusion holes, of 0.049-mm thickness, and with the following areas: hole 1, 0.596 mm^2; hole 2, 0.813 mm^2; hole 3, 0.862 mm^2. In each experiment the mass loss of the crystalline sample, Δm, was measured by weighing the cells with the samples to ±0.01 mg before and after a convenient effusion time, t, in a system evacuated to near 10^{-4} Pa. The cells were immersed in a thermostatically controlled oil bath. At temperature T, the vapor pressure, p, was calculated from the equation

$$p = (\Delta m/A_0W_0t)(2\pi RT/M)^{1/2}$$

in which M is the molar mass of the effusing vapor, A_0 is the area of the effusion hole, and W_0 is the Clausing factor, $W_0 = 1 + 3\lambda/8r^{-1}$ where λ is the thickness of the effusion hole and r its radius.

The Clausius–Clapeyron equation

$$\ln p/\text{Pa} = -\Delta^g_{cr}H^0_m(T_m)/RT + C$$

was used to derive the standard molar enthalpy of sublimation at the mean temperature, T_m, of the experimental range, by least-squares fitting of the results obtained with the three cells. The value was then corrected to 298.15 K using $\Delta^g_{cr}C^0_{p,m} = -50$ J K^{-1} mol^{-1} in accordance with estimations made by other authors.[15]

Results. Results for a typical combustion experiment on each compound are given in Table I; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the average mass assigned to ϵ(calor). Samples were ignited at 298.15 K so that $\Delta U(\text{IBP}) = -\{\epsilon(\text{calor}) + c_p(H_2O,l)\Delta m(H_2O) + \epsilon_f\}\Delta T_{ad} + \Delta U(\text{ign})$; ΔU_Σ is the correction to the standard state, and the remaining terms are as previously defined.[8] The individual values of $\Delta_c u^0$ with the mean and its standard deviation are given in Table II. Table III lists the derived standard molar enthalpies of combustion and of formation in the crystalline and gaseous states. In accordance with normal thermochemical practice, the uncertainties assigned to the derived molar enthalpies are twice the overall standard deviations of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_f H^0_m$ from $\Delta_c H^0_m$, the values $\Delta_f H^0_m$-

TABLE III: Derived Molar Values (kJ mol^{-1}) at 298.15 K

	$-\Delta_c U^0_m$(cr)	$-\Delta_c H^0_m$(cr)	$\Delta_f H^0_m$(cr)	$\Delta^g_{cr}H^0_m$	$\Delta_f H^0_m$(g)
MC	3076.5 ± 0.8	3079.0 ± 0.8	−425.4 ± 1.1	89.8 ± 1.1	−335.6 ± 1.6
PC	3094.3 ± 0.6	3096.8 ± 0.6	−407.6 ± 1.0	75.0 ± 1.0	−332.6 ± 1.2
4dmeMC	4358.5 ± 1.3	4363.5 ± 1.3	−499.6 ± 1.7	99.2 ± 2.1	−400.4 ± 2.7
5dmeMC	4374.7 ± 1.2	4379.7 ± 1.2	−483.4 ± 1.6	99.8 ± 1.1	−383.6 ± 1.9

TABLE IV: Vapor Pressure Results and Enthalpies of Sublimation

hole no.	a	b/K	T_m/K	$\Delta^g_{cr}H^0_m(T_m)$/kJ mol^{-1}	$\Delta^g_{cr}H^0_m$(298.15 K)/kJ mol^{-1}
			4demMC		
1	36.441 ± 0.455	11776 ± 144		97.9 ± 1.2	
2	36.168 ± 0.379	11712 ± 120		97.4 ± 1.0	
3	36.932 ± 0.487	11965 ± 154		99.5 ± 1.3	
global result	36.514 ± 0.785	11818 ± 249	317.18	98.2 ± 2.1	99.2 ± 2.1
			5dmeMC		
1	35.891 ± 0.302	11947 ± 98		99.3 ± 0.8	
2	35.177 ± 0.214	11729 ± 70		97.5 ± 0.6	
3	35.244 ± 0.161	11761 ± 52		97.8 ± 0.4	
global result	35.527 ± 0.412	11842 ± 134	325.65	98.4 ± 1.1	99.8 ± 1.1

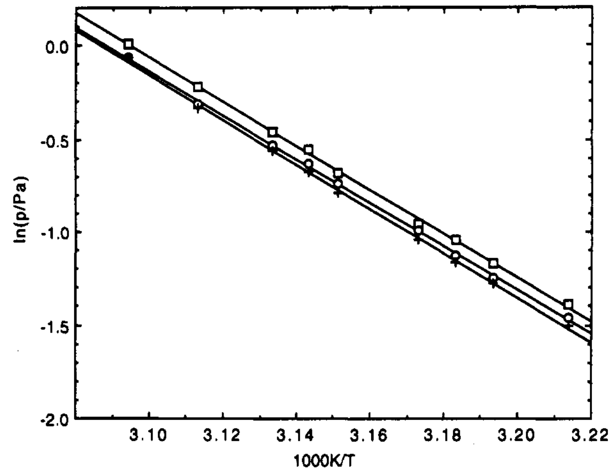

Figure 1. Plot of $\ln p/\mathrm{Pa} = f(T/\mathrm{K})$ for 4,4-dimethyl-1,3-cyclohexanedione: □, hole 1; ○, hole 2; +, hole 3.

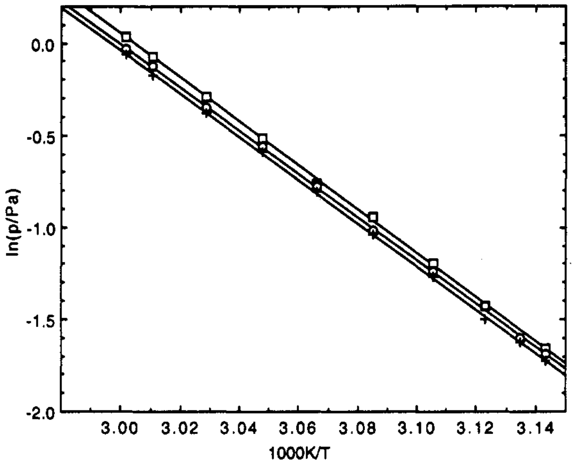

Figure 2. Plot of $\ln p/\mathrm{Pa} = f(T/\mathrm{K})$ for 5,5-dimethyl-1,3-cyclohexanedione: □, hole 1; ○, hole 2; +, hole 3.

$(H_2O,l)/\mathrm{kJ\ mol^{-1}} = -285.83 \pm 0.04$ and $\Delta_f H^0_m(CO_{2,g})/\mathrm{kJ\ mol^{-1}} = -393.51 \pm 0.13$ were used.[16]

The vapor pressure results (Table IV) give for each compound and each hole used the parameters of the Clausius–Clapeyron equation $\ln p/\mathrm{Pa} = a - b/(T/\mathrm{K})$, the mean temperature, T_m, of the experimental range, the enthalpy of sublimation at T_m, and the value corrected to 298.15 K. The plots of $\ln p/\mathrm{Pa}$ as $f(T)^{-1}$ are presented in Figures 1 and 2. Table V lists the (p,T) values calculated from the (p,T) equations derived for the two compounds within the experimental pressure range 0.2–1 Pa.

NMR Spectroscopy. Solid-state ^1H and ^{13}C NMR spectra were obtained at ambient temperature using a Varian Associates Unity 300 spectrometer operating at 300 MHz for protons. The magic-angle spinning probes were supplied by Doty Scientific Inc. Proton CRAMPS spectra (combined rotation and multiple-pulse spectra) were obtained at a spinning speed of 1.6 kHz using the MREV8 pulse seqeunce[17] for removal of homonuclear dipolar coupling. The chemical shift scale was referenced by setting the main CH_2 peak to 1.5 ppm. ^{13}C spectra were obtained using the standard CPMAS technique (cross-polarization/magic-angle spinning) with a contact time of 1 ms, a spinning speed of 4 kHz, and a recycle time of 3 s. Spectra were referenced using a separate adamantane sample.

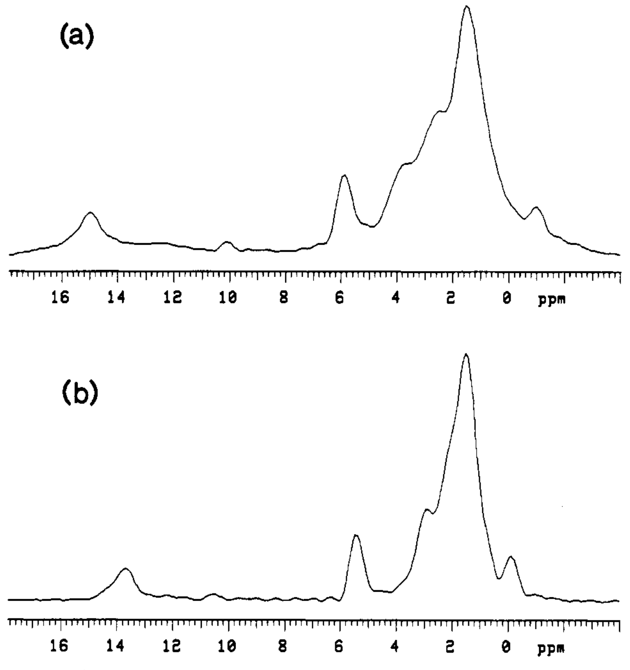

Figure 3. ^1H CRAMPS spectra of (a) 5,5-dimethyl-1,3-cyclohexanedione and (b) 4,4-dimethyl-1,3-cyclohexanedione.

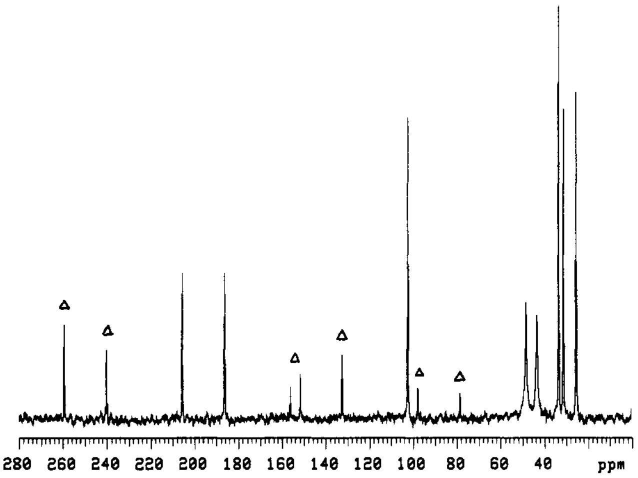

Figure 4. ^{13}C CPMAS spectrum of 5,5-dimethyl-1,3-cyclohexanedione at spinning speed of 4 kHz. The symbol Δ indicates a spinning sideband.

Figure 3 shows the ^1H CRAMPS spectra of 4dmeMC and 5dmeMC. Both spectra show an expected intense broad peak from the CH_2 and CH_3 groups in the region 1–3 ppm, but additionally there are peaks at ca. 5.5 and 14–15 ppm: the former is attributable to olefinic protons while the latter is attributable to strongly hydrogen-bonded protons.[18]

Figure 4 shows the ^{13}C CPMAS spectrum of 5dmeMC. This spectrum shows a peak at 101 ppm characteristic of an olefinic carbon and two peaks at 186 and 206 ppm characteristic of carbonyl carbons.[19]

Both ^1H and ^{13}C spectra show clearly that these dimethylcyclohexanediones exist in the enol form in the solid state.

Ab Initio Calculations. Unconstrained geometry optimizations on all the five forms shown in Figure 5 were performed using a split valence basis set augmented with polarization functions on all atoms (SV 6-31G**),[20] using the quantum mechanical program

TABLE V: *T* and *p* Values from the Vapor Pressure Equations

	p/Pa								
	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T(4dmeMC)/K	309.99	313.27	315.68	317.57	319.14	320.47	321.64	322.67	323.66
T(5dmeMC)/K	318.87	322.39	324.94	326.94	328.59	330.00	331.24	332.33	333.32

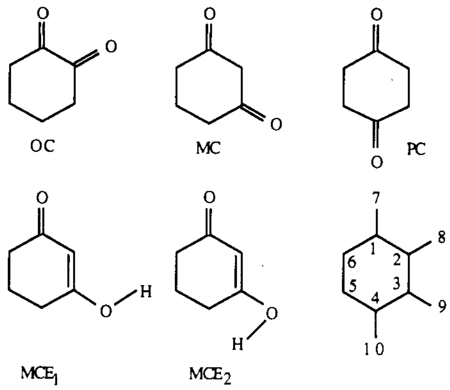

Figure 5. Structures of cyclohexanediones and enol forms.

GAMESS. Such large basis sets are capable of closely predicting molecular structure, bond lengths to ±0.02 Å and bond angles to ±1–2°, and relative gas-phase energetics for organic molecules having conventional bonding to about ±4 kJ mol^{-1}.

The optimized structures for the five species are given in Table VI. From an X-ray investigation[21] structural data are available for MCE1 and are also listed in Table VI. Although a direct comparison of calculated and crystallographic structures must be treated cautiously due to intermolecular hydrogen bonding and other solid-state effects, the agreement with the results from X-ray analysis is satisfactory. All five species are predicted to be nonplanar with the enolic forms in a sofa conformation and MC and OC to be in a chairlike conformation. The PC isomer is one in which two low-energy structures are possible: the extended skew and the chair conformations. Although the extended skew form is favored in the solid phase and in solution,[22,23] molecular beam studies by Dowd et al.[24] lead these authors to suggest the chair form is dominant in the gaseous phase.

Indeed, we predict the chair form to be 2.0 kJ mol^{-1} lower in energy than the extended skew isomer. Thus, it is the chair form of PC for which theoretical predictions are made.

Table VII reports the total and relative energies of the isomers. The predicted enthalpy of isomerization of the PC and MC pair, 1.6 kJ mol^{-1}, is in agreement with the experimental value, 3.0 ± 2.0 kJ mol^{-1}, the MC form being the lower energy isomer. As expected, the OC form is predicted to be the highest energy isomer, lying ca. 36 kJ mol^{-1} above the MC isomer. The enolic forms of MC are both predicted to be less stable than the diketo form, in agreement with the photoelectron study.[25] In these calculations we have not considered zero-point corrections to the predicted energetics due to computational limitations. However, these are expected to be small as far as the predicted isomerization energies are concerned. For the keto–enol tautomerism, the contribution is expected to be less than 1 kJ mol^{-1} based upon theoretical and experimental studies of the 2-hydroxypyridine/2(1*H*)-pyridone system.[26]

TABLE VII: Calculated Total and Relative Energies

	total energy/au	relative energy/kJ mol^{-1}
OC	−381.599 418	35.7
MC	−381.613 003	0.0
PC	−381.612 386	1.6
MCE1	−381.606 103	18.1
MCE2	−381.601 348	30.6

Discussion

1,3-Cyclohexanedione derivatives change structure between the crystalline and gaseous states; in the crystalline state they exist as enol tautomers as demonstrated by the NMR spectra of 4dmeMC and 5dmeMC. Crystal structures have been reported for 5dmeMC[27] in which the molecules are arranged in a helix with the O–H- -O intermolecular hydrogen bond distance of 2.595 Å, and for MC, a chain structure (anti–anti) in which the hydrogen bond distance is 2.561 Å.[21] Consequently, the intermolecular hydrogen bond energy in the crystal must exceed the enthalpy of isomerization to the enol form. This conclusion is supported by the fact that the O–H- -O distance in the dimer of ethanoic acid is 2.76 Å,[28] significantly longer than the corresponding distance in the crystals of 1,3-cyclohexanedione derivatives, and the intermolecular hydrogen bond energy in ethanoic acid dimer is 30.3 ± 2.3 kJ mol^{-1}.[29]

If the calculated enthalpy of enolization of 1,3-cyclohexanedione to the syn-enol form is assumed to be the appropriate value for enolization of a β-diketone without an intramolecular hydrogen bond, then, as for 2,4-pentanedione, the enol form has been determined to be 10 kJ mol^{-1} more stable than the keto form in the gaseous state;[30] the intramolecular hydrogen bond energy in 2,4-pentanedione is estimated to be 28 kJ mol^{-1}, a not unexpected value.

TABLE VI: Optimized Bond Lengths and Bond Angles (Heavy Atoms)[a]

	r/Å				
	OC	MC	PC	MCE1[b]	MCE2
1–2	1.534	1.521	1.517	1.470 (1.413)	1.469
2–3	1.512	1.521	1.539	1.335 (1.350)	1.331
3–4	1.538	1.515	1.517	1.500 (1.490)	1.505
4–5	1.533	1.537	1.517	1.526 (1.511)	1.528
5–6	1.538	1.537	1.540	1.526 (1.514)	1.527
6–1	1.512	1.515	1.517	1.519 (1.496)	1.519
7–1	1.188	1.190	1.191	1.198 (1.252)	1.198
8–2	1.188				
9–3		1.190		1.336 (1.316)	1.341
10–4			1.191		

	Γ/deg				
	OC	MC	PC	MCE1	MCE2
1–2–3	114.2	107.4	111.8	121.6 (121.7)	121.9
2–3–4	111.1	115.3	111.8	123.6 (122.4)	123.7
3–4–5	122.4	111.2	115.2	111.2 (111.4)	111.7
4–5–6	112.7	112.4	112.2	110.7 (111.4)	111.1
6–1–2	114.3	115.3	115.2	117.1 (113.0)	116.9
7–1–2	121.0	121.6	122.4	121.7 (119.2)	121.9
8–2–3	114.2				
9–3–4		123.1		112.0 (114.0)	116.7
3–9–H(O)				111.6 (112.5)	111.8
10–4–5			122.3		

[a] See Figure 5 for atom numbering. [b] Experimental values (ref 21) are in parentheses.

From the calculated enthalpy of isomerization of 1,3-cyclohexanedione to 1,2-cyclohexanedione, the enthalpy of formation of the latter in the gaseous state is predicted to be -300 ± 5 kJ mol^{-1}. From the gaseous enthalpies of formation and values calculated for strain-free structures using the Laidler bond energy scheme with parameters given in ref 31, the following conventional strain energies (in kJ mol^{-1}) were derived: 1,2-cyclohexanedione, 13.8; 1,3-cyclohexanedione, 13.6; 1,4-cyclohexanedione, 17.2; 4,4-dimethyl-1,3-cyclohexanedione, 13.5; 5,5-dimethyl-1,3-cyclohexanedione, 28.9. The higher value in the last compound can be ascribed to a close approach of hydrogen atoms on carbon atoms 1 and 5 apart, on a methyl group, and on the carbon between the two carbonyl groups. These conventional strain energies fall into an expected pattern.

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