J. Phys. Chem. A **2007,** *111,* 11153−11159

Calorimetric and Computational Study of Indanones

**M. Agostinha R. Matos,[†] Margarida S. Miranda,[†] Manuel J. S. Monte,[†]
Luís M. N. B. F. Santos,[†] Victor M. F. Morais,[†,‡] James S. Chickos,[||]
Patamaporn Umnahanant,[||] and Joel F. Liebman*[,§]**

Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal, Instituto de Ciências Biomédicas Abel Salazar, ICBAS, Universidade do Porto, P-4099-003 Porto, Portugal, Department of Chemistry and Biochemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121, and Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, Maryland 21250

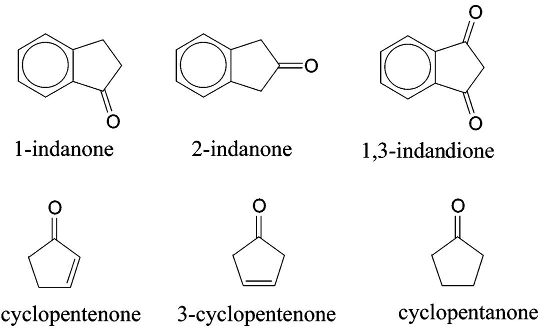
Received: June 18, 2007; In Final Form: August 21, 2007

Condensed phase standard ($p° = 0.1$ MPa) molar enthalpies of formation for 1-indanone, 2-indanone, and 1,3-indandione were derived from the standard molar enthalpies of combustion, in oxygen, at $T = 298.15$ K, measured by static bomb combustion calorimetry. The standard molar enthalpies of sublimation for 1-indanone and 2-indanone, at $T = 298.15$ K, were measured both by correlation-gas chromatography and by Calvet microcalorimetry leading to a mean value for each compound. For 1,3-indandione, the standard molar enthalpy of sublimation was derived from the vapor pressure dependence on temperature. The following enthalpies of formation in gas phase, at $T = 298.15$ K, were then derived: 1-indanone, -64.0 ± 3.8 kJ mol^{-1}; 2-indanone, -56.6 ± 4.8 kJ mol^{-1}; 1,3-indandione, -165.0 ± 2.6 kJ mol^{-1}. The vaporization and fusion enthalpies of the indanones studied are also reported. In addition, theoretical calculations using the density functional theory with the B3LYP and MPW1B95 energy functionals and the 6-311G** and cc-pVTZ basis sets have been performed for these molecules and the corresponding one-ring species to obtain the most stable geometries and to access their energetic stabilities.

Introduction

Although indole and its derivatives are well-known to have considerable biomedical activity ranging from the amino acid tryptophan and the plant auxin, indole-3-acetic acid, to the psychopharmacologically active melatonin and serotonin, perhaps generally less appreciated, the related carbocycles indene, indan, and their derivatives such as substituted 1-indanones (2,3-dihydro-1*H*-inden-1-one) also have a wide range of biomedical applications.[1] The study of the acidity of 2-indanone provided seminal information as to the effects of phenyl groups on the acidification of ketones,[2] and thereby led to insights into the physical bioorganic chemistry of unsaturated ketones, in particular steroids such as testosterone.[3] Indoles and indans also appear on both sides of the legal fulcrum: the illicit drug LSD is an indole derivative. 1,2,3-Indantrione enjoys considerable criminological importance: its covalent hydrate is better known as ninhydrin, an important reagent for fingerprint detection at crime scenes.[4] Despite these enunciated applications, there has been little work reported regarding the structure and energetics of carbonyl-containing indene compounds.

SCHEME 1: Structures of the Compounds Studied



In the present work we report the standard molar enthalpies of formation of three indanones, 1-indanone, 2-indanone, and 1,3-indandione in the gaseous phase (Scheme 1). The remaining indanones, 1,2-indandione and 1,2,3-indantrione, were not studied as they are not available in pure and/or anhydrous form. This is in contradistinction to 2,3-indoledione, also known as isatin, and investigated by us earlier, calorimetrically.[5] As in this last study, our current results were obtained from measurements of combustion energies using a static bomb calorimeter. The enthalpies of sublimation were measured by Calvet microcalorimetry and by correlation-gas chromatography (1- and 2-indanone) or derived from the vapor pressure dependence on temperature (1,3-indandione). Density functional theory calculations were also performed for these two-ring molecules and for the related one-ring cyclopentanone and 2- and 3-cyclopentenone. There is good agreement between experimentally and theoretically calculated enthalpies of isodesmic reactions.

Experimental Section

The compounds studied were obtained commercially from Aldrich Chemical Co with the assigned mass fraction purities

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* Corresponding author. E-mail jliebman@umbc.edu. Phone: -1-410-455-2549. Fax: -1-410-455-2608.

[†] Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto.

[‡] ICBAS, Universidade do Porto.

[||] University of Missouri—St. Louis.

[§] University of Maryland.

10.1021/jp074718d CCC: $37.00

of: 1-indanone [83-33-0] 99.90%, 2-indanone [615-13-4] 98.20%, and 1,3-indandione [606-23-5] 99.5% determined by gas−liquid chromatography. The compounds were further purified by repeated sublimation before the calorimetric measurements. The final purity of 1- and 2-indanone was assessed by DSC analysis using the fractional fusion technique.[6] 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}. No phase transitions were observed between $T = 298.15$ K and the fusion temperature. 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:[7] naphthalene, benzoic acid, and indium.

The composition of the crystalline samples was also assessed through the carbon dioxide recovery ratio. The average ratios of the mass of carbon dioxide recovered to that calculated from the mass of sample, together with the standard deviation of the mean, were 1-indanone, 100.00 ± 0.03, 2-indanone, 100.04 ± 0.03, and 1,3-indandione, 100.00 ± 0.02. The specific densities of the samples were taken from ref 8 as $\rho = 1.103$ g cm^{-3} (1-indanone), $\rho = 1.0712$ g cm^{-3} (2-indanone), and $\rho = 1.37$ g cm^{-3} (1,3-indandione).

Combustion Calorimetry Measurements

The energies of combustion of the compounds were measured using a static bomb calorimeter. Because the apparatus and the technique have been described;[9,10] 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 $\Delta_c u = -26435.1 \pm 3.5$ 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: $\epsilon_{\mathrm{cal}} = 16005.0 \pm 2.0$ J K^{-1}, where the uncertainty quoted is the standard deviation of the mean.

For all experiments, the samples were ignited at $T = 298.150 \pm 0.001$ K in oxygen, at a pressure of 3.04 MPa, with a volume of water of 1.00 cm^3 added to the bomb.

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 $\Delta_c u^\circ = -16240$ J g^{-1},[11] 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},[12] 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 crystalline 1- and 2-indanone were enclosed in polyester bags made of Melinex, using the technique described by Skinner and Snelson,[13] 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 with the factor previously reported.[13] In the combustion experiments of 1,3-indandione, *n*-hexadecane (Aldrich Gold Label, mass fraction >0.99) was used to moderate and to make the combustions complete. Its standard massic energy of combustion was measured separately to be $\Delta_c u^\circ = -47160.8 \pm 4.1$ J g^{-1}.

The mass of compound, *m*(compound), used in each experiment was determined from the total mass of carbon dioxide, $m(CO_2,\mathrm{total})$, produced after allowance for that formed from the cotton thread fuse, Melinex and *n*-hexadecane.

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 organic compounds, was assumed.[14] For each compound, the 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.[15]

Calvet Microcalorimetry Experiments

The standard molar enthalpies of sublimation were measured using the "vacuum sublimation" drop microcalorimetric method,[16] a method shown to be in good agreement with other sublimation methods, e.g., ref 16. Samples of 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. An empty capillary tube was dropped in the reference calorimetric cell, simultaneously. 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}.[17] Accuracy tests were performed with benzoic acid.

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

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

where *T* is the temperature of the hot reaction vessel and $C_{p,\mathrm{m}}^{\circ}(\mathrm{g})$ is the molar heat capacity of the gaseous compound. The heat capacity and its temperature dependence for 1-indanone, 2-indanone, and 1,3-indandione, respectively,

$$C_{p,\mathrm{m}}^{\circ}(\mathrm{g})/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -0.000326(T/\mathrm{K})^2 + 0.682(T/\mathrm{K}) - 43.418 \qquad (2)$$

$$C_{p,\mathrm{m}}^{\circ}(\mathrm{g})/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -0.000345(T/\mathrm{K})^2 + 0.697(T/\mathrm{K}) - 44.714 \qquad (3)$$

$$C_{p,\mathrm{m}}^{\circ}(\mathrm{g})/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -0.000366(T/\mathrm{K})^2 + 0.684(T/\mathrm{K}) - 32.974 \qquad (4)$$

were derived from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP functional and the 6-31G* basis set. As expected from the success of group incremental methods for estimating heat capacities,[17] the coefficients for $(T/\mathrm{K})^2$, (T/K), and the constant term are found to be very nearly the same for 1- and 2-indanone.

The atomic weights of the elements were those recommended by the IUPAC commission.[18]

Vapor Pressure Measurements

The vapor pressures of crystalline 1,3-indandione were measured at different temperatures using a static apparatus based on a capacitance diaphragm gage. The apparatus has been tested by measurements of vapor pressure of recommended reference compounds (naphthalene, benzoic acid, benzophenone, and ferrocene) and proved to provide reliable vapor pressure data as well as accurate values of enthalpies of sublimation or

TABLE 1: Experimental Vapor Pressures of Sublimation, p, of 1,3-Indandione

T/K	p/Pa	Δp/Pa[a]
320.47	0.663	−0.0006
322.95	0.864	−0.0032
325.44	1.135	0.0059
327.92	1.464	0.0023
330.43	1.903	0.0136
332.88	2.403	−0.0136
335.37	3.095	0.005
337.85	3.933	0.0026
340.34	4.977	−0.0066
342.82	6.303	0.0154
345.30	7.903	0.0014
347.78	9.893	0.0012
350.28	12.283	−0.0758
352.75	15.293	−0.0506
355.22	19.013	0.0315
357.71	23.543	0.1032

[a] $\Delta p = p - p_{\mathrm{calc}}$, where p_{calc} is calculated from the Clarke and Glew equation and the derived parameters $\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^0$, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^0$, and $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$.

vaporization.[19] The uncertainty in the pressure measurements is adequately described by the equation $\sigma(p/\mathrm{Pa}) = 0.01 + 0.0025(p/\mathrm{Pa})$, and the workable temperature and pressure ranges are 243−413 K and 0.4−133 Pa, respectively.

The thermodynamic parameters of the sublimation of 1,3-indandione, $\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^0$, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^0$, and $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$, were derived by fitting the Clarke and Glew equation (eq 5) to the vapor pressure results presented in Table 1.

$$R \ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^0(\theta)}{\theta} + \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^0(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^0(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (5)$$

In this equation, p is the vapor pressure at the temperature T, $p°$ is a selected reference pressure (in this work we took $p^0 = 10^5$ Pa), θ is a selected reference temperature (in this work we took $\theta = 298.15$ K), R is the molar gas constant ($R = 8.314\,472$ J K^{-1} mol^{-1}), and $\Delta_{\mathrm{cr}}^{\mathrm{g}} G_{\mathrm{m}}^0$, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^0$, and $\Delta_{\mathrm{cr}}^{\mathrm{g}} C_{p,\mathrm{m}}^0$ are the differences, at the selected reference pressure, between the gaseous and the crystalline phase, respectively, in the molar Gibbs energy, the molar enthalpy, and the molar heat capacity of 1,3-indandione.

The static apparatus used and the measuring procedure have been recently described in detail,[19] so only a short description is given here. The pressure measuring device is a capacitance diaphragm absolute gage MKS Baratron 631A01TBEH, with a measuring upper limit of 133 Pa and an uncertainty of 0.25% of the reading pressure, as stated by the manufacturer. The temperature of the pressure sensor is kept at $T = 423$ K by the self-controlling temperature system. The pressure gage has been calibrated at 423 K by the manufacturer. This calibration is traceable to the National Institute of Standards and Technology (NIST). The tubing system was constructed using stainless steel tubing of internal diameter 17 mm with connections ConFlat DN 16 CF and includes all metal angle valves, VAT series 57 high-temperature range for UHV, operated pneumatically.

The sample cell is essentially a stainless steel tube (120 mm long and 12 mm external diameter), which is inserted in a metal cavity where the temperature is controlled by a double-jacked copper cylinder with a circulating fluid from a thermostatic bath, Julabo F33-MW. The temperature of the sample is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four-wire connection), which is in good thermal contact with the sample. This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be less than ±0.01 K. All temperatures reported here are based on the international temperature scale ITS-90.

Vaporization Enthalpies Measurements

Vaporization enthalpies were measured by correlation-gas chromatography. This technique has also been detailed previously,[20] so only a brief description need be given here. The technique consists of measuring the retention times of a series of structurally related compounds with known vaporization enthalpies, along with the compounds whose vaporization enthalpy is of interest, as a function of temperature, along with a standard which is not retained by the column. Depending on temperature, this material can be the solvent or, frequently, methane is used as the nonretained reference. The difference in retention time between each analyte, and the nonretained reference is the amount of time the analyte spends on the column, t_{a}. The quantity t_{a} is inversely proportional to the compounds vapor pressure. A plot of $\ln(t_{\mathrm{o}}/t_{\mathrm{a}})$ against $1/T$ (K^{-1}), where t_{o} is a reference time, 1 min, results in a straight line whose slope measures the enthalpy of transfer of the solute from the stationary phase of the column to the gas phase divided by the gas constant. The enthalpy of transfer, $\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}})$, is a sum of the vaporization enthalpy of the analyte and its enthalpy of interaction with the column at the mean temperature of measurement, T_{m}. Provided the structure of the reference materials are properly selected, $\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(T_{\mathrm{m}})$ is found to correlate linearly with the vaporization enthalpy of reference materials at $T = 298.15$ K. A summary of the correlations obtained for 1- and 2-indanone and for 1,3-indandione is presented in Tables S2, S4, and S6 in the Supporting Information and eqs 6−8, respectively. Retention times and literature references of the standards as well as some additional experimental information are provided in the Supporting Information.

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.156 \pm 0.074)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(402\ \mathrm{K}) + (10.05 \pm 1.39) \quad (r^2 = 0.9879) \quad (6)$$

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.153 \pm 0.074)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(419\ \mathrm{K}) + (10.194 \pm 1.40) \quad (r^2 = 0.9878) \quad (7)$$

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (0.548 \pm 0.006)\Delta_{\mathrm{sln}}^{\mathrm{g}} H_{\mathrm{m}}(419\ \mathrm{K}) + (49.13 \pm 1.0) \quad (r^2 = 0.9999) \quad (8)$$

Computational Details

The geometries of the compounds studied were fully optimized using density functional theory (DFT) with the Becke three-parameter hybrid exchange[22] and Lee−Yang−Parr[23] correlation density functional (B3LYP) and two different basis sets: 6-31G*[24] and 6-311G**.[25] 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 to obtain the corrections needed to derive energies at the temperature of $T = 298.15$ K. More accurate

TABLE 2: Summary of the DSC Results

compound	$\Delta_{cr}^{l}H_m(T_{fus})$/ (kJ mol^{-1})	T_{fus}/K	C_p(l)^c/ (J mol^{-1} K^{-1})	C_p(cr)^c/ (J mol^{-1} K^{-1})	$\Delta_{cr}^{l}H_m^\circ$(298.15 K)/ (kJ mol^{-1})^d	mol %
1-indanone	17.6 ± 0.22 17.8^a	314.14 ± 0.04 312.9^a	216	170.5	17.0 ± 0.2	99.98 ± 0.02
2-indanone	16.89 ± 0.21	329.95 ± 0.13	216	170.5	15.6 ± 0.4	99.90 ± 0.04
1,3-indandione	21.8 ± 0.15^b	401.5	236.5	180.2	17.2	decomposes on fusion

[a] Reference 21. [b] Triplicate run with slight decomposition; measured in St. Louis. [c] Estimated by group additivity.[17] [d] Adjusted to $T = 298.15$ K using eq 9.

energies were also obtained from single-point calculations at the most stable B3LYP/6-311G** geometries, using the triple-ζ correlation consistent basis set, cc-pVTZ,[26] and also with the MPW1B95[27] density functional using the 6-311G** and cc-pVTZ basis sets. All calculations were performed using the UK version of GAMESS,[28,29]except the calculations with the density functional MPW1B95 which were performed with the Gaussian 03 series of programs.[30]

Experimental Results

DSC Results. The purity of the compounds was assessed using differential scanning calorimetry (DSC) except for 1,3-indandione, which decomposes slightly during the fusion process. 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 2. The uncertainties assigned to the results are twice the standard deviation of the mean of five independent runs.

Some decomposition of 1,3-indandione was indicated by the fact that upon cooling and reheating, both the enthalpy and peak shape deteriorated slightly. Though most organic compounds show slightly smaller fusion enthalpies upon reheating, continuous recycling clearly indicated decomposition. Slight decomposition is also indicated by the sublimation enthalpy calculated from the sum of the vaporization and fusion enthalpies discussed below.

Fusion enthalpies were adjusted to $T = 298.15$ K using the following equation:[31]

$$\Delta_{cr}^{l}H_m^\circ(298.15\ \text{K})/\text{kJ·mol}^{-1} = \Delta_{cr}^{l}H_m^\circ(T_{fus}) + [0.15C_p(\text{cr}) - 0.26C_p(\text{l}) - 9.83]\quad (T_m - 298.15)/1000 \quad (9)$$

Heat capacities of the solid, C_p(cr), and liquid phase, C_p(l), were estimated and an uncertainty of one-third of the temperature adjustment was arbitrarily assigned.

Combustion Calorimetry Results. Results for a typical combustion experiment of each compound are given in Table 3. The symbols in this table have the same meaning as in ref 15. As samples were ignited at $T = 298.15$ K,

$$\Delta U(\text{IBP}) = -\{\epsilon_{cal} + c_p(\text{H}_2\text{O,l})\Delta m(\text{H}_2\text{O}) + \epsilon_f\}\Delta T_{ad} + \Delta U(\text{ign}) \quad (10)$$

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 increase raise calculated using the program LABTERMO,[32] and ΔU_{ign} is the energy of ignition.

TABLE 3: Typical Combustion Experiments at $T = 298.15$ K^a

	1-indanone	2-indanone	1,3-indandione
$m(CO_2$, total)/g	2.05575	1.81146	2.30867
m(compound)/g	0.64130	0.56385	0.61578
m(fuse)/g	0.00216	0.00223	0.00214
m(n-hexadecane)/g			0.20462
m(Melinex)/g	0.05689	0.05153	
ΔT_{ad}/K	1.45961	1.28760	1.69364
ϵ_f/(J K^{-1})	16.29	15.82	16.85
$\Delta m(H_2O)$/g	0.0	0.0	0.0
$-\Delta U$(IBP)/J	23383.65	20627.21	27134.06
ΔU(fuse)/J	35.08	36.22	34.75
ΔU(n-hexadecane)/J			9650.20
ΔU(Melinex)/J	1302.84	1180.16	
$\Delta U(HNO_3)$/J	6.87	3.56	0.24
ΔU(carbon)/J	0.00	0.00	0.00
ΔU(ign.)/J	1.19	1.20	1.19
ΔU_Σ/J	14.35	12.43	15.84
$-\Delta_c u^\circ$/(J g^{-1})	34343.54	34397.16	28310.48

[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(n-hexadecane) is the mass of n-hexadecane 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(ignition); ΔU(fuse) is the energy of combustion of the fuse (cotton); ΔU(n-hexadecane) is the energy of combustion of n-hexadecane; ΔU(Melinex) is the energy of combustion of Melinex; $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(carbon) is the energy correction for carbon formation; ΔU_Σ is the energy correction to the standard state; $\Delta_c u^\circ$ is the standard massic energy of combustion.

TABLE 4: Derived Standard ($p^\circ = 0.1$ 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)
1-indanone	−4539.2 ± 2.3	−4542.9 ± 2.3	−142.0 ± 2.6
2-indanone	−4548.2 ± 2.7	−4551.9 ± 2.7	−133.0 ± 2.9
1,3-indandione	−4137.9 ± 2.2	−4139.1 ± 2.2	−260.0 ± 2.5

The individual results of the massic energies 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 S8 of Supporting Information. 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,[33] 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 the 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} [34] and −393.51 ± 0.13 kJ mol^{-1}.[34]

TABLE 5: Calorimetric Standard ($p° = 0.1$ MPa) Molar Enthalpies of Sublimation, at $T = 298.15$ K (kJ mol^{-1})

compound	no. of expts	T/K	$\Delta_{\mathrm{cr,298.15\,K}}^{\mathrm{g,T}}H_{\mathrm{m}}^{\circ}$	$\Delta_{\mathrm{298.15K}}^{\mathrm{T}}H_{\mathrm{m}}^{\circ}(\mathrm{g})$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$ (298.15 K)
1-indanone	9	365	88.5 ± 2.8	9.8	78.7 ± 2.8
2-indanone	6	365	88.2 ± 1.1	9.9	78.3 ± 1.1
1,3-indandione	6	365	107.6 ± 1.8	10.3	97.3 ± 1.8

TABLE 6: Summary of Fusion, Vaporization, and Sublimation Enthalpies by Correlation-Gas Chromatography (kJ mol^{-1})

compound	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{m}^{\circ}$ (298)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{m}^{\circ}$(298)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{m}^{\circ}$(298)
1-indanone	17.0 ± 0.2	60.4 ± 2.8	77.4 ± 2.8
2-indanone	15.6 ± 0.4	58.9 ± 2.8	74.5 ± 2.8
1,3-indandione	17.2[a]	72.6 ± 2.0	89.8

[a] This result for 1,3-indandione assumes the material is stable at its fusion temperature.

TABLE 7: 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	$\Delta_{\mathrm{f}}H_{m}^{\circ}$(cr)	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{m}^{\circ}$	$\Delta_{\mathrm{f}}H_{m}^{\circ}$(g)
1-indanone	−142.0 ± 2.6	78.0 ± 1.3	−64.0 ± 3.8
2-indanone	−133.0 ± 2.9	76.4 ± 3.8	−56.6 ± 4.8
1,3-indandione	−260.0 ± 2.5	95.0 ± 0.7	−165.0 ± 2.6

Calvet Microcalorimetry, Correlation-Gas Chromatography, and Vapor Pressure Results. The standard molar enthalpies of sublimation of the three indanones were measured by Calvet microcalorimetry. The experimental results are given in Table 5 for the three compounds with uncertainties of twice the standard deviation of the mean. For 1- and 2-indanone the standard molar enthalpy of sublimation was also obtained by correlation-gas chromatography and the results are summarized in Table 6.

The calorimetric results are in good agreement with the results obtained by correlation-gas chromatography for both 1- and 2-indanone but are in serious disagreement with the results for 1,3-indandione. This factor prompted us to examine the fusion process discussed above and to measure the sublimation enthalpy by a third independent method. The results, evaluated by measuring the vapor pressure of sublimation of 1,3-indandione as a function of temperature using a capacitance diaphragm gage and derived by fitting the data to the Clarke and Glew equation (eq 5), are $\Delta_{\mathrm{cr}}^{\mathrm{g}}\,G_{\mathrm{m}}^{0}/(\mathrm{J\ mol^{-1}}) = 36095 \pm 40$, $\Delta_{\mathrm{cr}}^{\mathrm{g}}\,H_{\mathrm{m}}^{0}/(\mathrm{kJ\ mol^{-1}}) = 95.0 \pm 0.7$, and $\Delta_{\mathrm{cr}}^{\mathrm{g}}\,C_{p,\mathrm{m}}^{0}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = -93 \pm 16$. Experimental details are provided in the Experimental Section.

The experimental sublimation enthalpy measured at temperatures where the crystalline phase is stable is consistent with the DSC observations that 1,3-indandione decomposes slightly at its melting point, resulting in a slight exotherm that reduces the observed fusion enthalpy. With the sublimation enthalpy measured by the capacitance diaphragm and the vaporization enthalpy measured by correlation-gas chromatography, a value of 22.4 ± 2.0 kJ mol^{-1} is calculated for the fusion enthalpy of 1,3-indandione in the absence of decomposition.

The derived standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, are summarized in Table 7. In the case of 1- and 2-indanone, values for the enthalpy of sublimation correspond to the mean of the Calvet and correlation-gas chromatography results, whereas for 1,3-indandione the enthalpy of sublimation value, at $T = 298.15$ K, obtained from the vapor pressure measurements was selected. This value was selected on the basis of its smaller uncertainty compared to the calorimetric value. The uncertainties associated with the sublimation enthalpies for 1-, and 2-indanone represent two standard deviations of the mean.

For 1-indanone, Verevkin[21] reported the standard enthalpies of formation in the crystalline and gaseous phases, respectively, of −145.25 ± 0.87 kJ mol^{-1} and −61.7 ± 1.1 kJ mol^{-1}, using a standard enthalpy of sublimation of 83.51 ± 0.73 kJ mol^{-1}. Our results are in good agreement with these values.

Theoretical Results and Discussion

The geometries of the compounds studied have been fully optimized using the B3LYP density functional and the 6-31G* and 6-311G** extended basis sets. The most relevant geometrical parameters obtained using the higher basis set are shown in Tables S9 and S10 (Supporting Information), respectively, for the two- and one-ring molecules (see Figures 1 and 2 in the Supporting Information for the numbering of the atoms). The three indanone molecules studied are found to be planar. The molecular structure of 1-indanone was previously studied using both RHF and DFT, with the B3LYP and BLYP density functionals, and with different basis sets;[1] a planar structure was also found. Among the most telling geometric parameters are the considerably shorter "C sp^2−CO" bonds in 1-indanone, 1,3-indandione, and 2-cyclopentenone, than the "C sp^3−CO" bonds in these species, and in 2-indanone, 3-cyclopentenone, and cyclopentanone.

Also shown in Table S9 are the relevant bond lengths and angles as measured by X-ray crystallography for 1-indanone[1] and for 1,3-indandione.[35] The calculated geometrical parameters are in generally good agreement with the experimental values.

Autrey and Laane[36] studied a number of cyclopentene-like molecules using high-level *ab initio* calculations. 3-Cyclopentenone was found to be a planar molecule because this molecule lacks $CH_2{-}CH_2$ torsional interactions. 2-Cyclopentenone does have such a $CH_2{-}CH_2$ interaction, but this is not sufficient to overcome the stabilizing conjugation between the C═O and C═C groups, erstwhile shown by solution phase hydrogenation calorimetry[37] and by direct isomer equilibration.[38] Hence, 2-cyclopentenone is also planar. A similar explanation is

TABLE 8: Calculated Reaction Energies at $T = 0$ K and Enthalpies at $T = 298.15$ K (kJ mol^{-1})

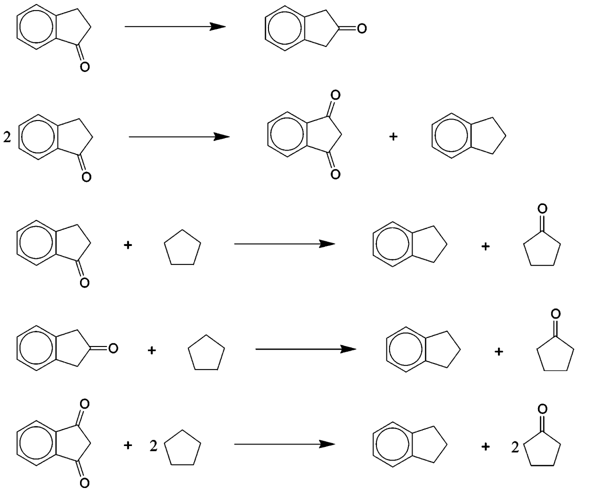
	$\Delta_{\mathrm{r}}E_{\mathrm{T}} = 0$ K				$\Delta_{\mathrm{r}}H_{T=298.15\,\mathrm{K}}^{\circ}$				
	B3LYP		MPW1B95		B3LYP		MPW1B95		
reaction	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	exp[a]
11	17.1	16.5	15.6	15.3	14.8	14.2	13.3	13.1	7.4 ± 6.1
12	18.8	19.6	18.0	18.6	18.2	18.9	17.4	18.0	23.7 ± 6.9
13	10.4	9.2	6.9	6.2	8.5	7.2	5.0	4.3	9.0 ± 6.4
14	−6.7	−7.3	−8.6	−9.1	−6.4	−7.0	−8.3	−8.8	1.6 ± 7.1
15	2.1	−1.2	−4.1	−6.1	−1.2	−4.5	−7.3	−9.4	−5.7 ± 8.5

[a] The experimental values of the enthalpies of formation of auxiliary molecules were taken from ref 40.

applicable to the understanding of the structure of the bicyclic molecules 1-indanone and 1,3-indandione, because of the expected conjugation between the C═O and the benzenoid ring.

Single point energy calculations were performed with the correlation-consistent cc-pVTZ basis set, using the optimized B3LYP/6-311G** geometries, and also with the MPW1B95 functional using the 6-311G** and the cc-pVTZ basis sets. The resulting electronic energies are shown in Table S11 under the appropriate headings, as well as the thermal corrections to $T = 298.15$ K. In this table we also show the corresponding energies of some auxiliary molecules. Comparison of our experimental enthalpies of formation in the gaseous phase and the theoretical calculations for the two isomeric indanones shows that 1-indanone is energetically more stable than the 2-isomer. This presumably arises from the conjugation between the C═O and the benzenoid ring in the 1-indanone isomer, a stabilizing mechanism absent in the 2-indanone isomer.[39]

To evaluate the accuracy of the calculations, we have considered the following isodesmic reactions:



(11)

(12)

(13)

(14)

(15)

The reaction energies at $T = 0$ K and enthalpies at $T = 298.15$ K are presented in Table 8, together with the corresponding experimental results (the experimental standard molar enthalpies of formation of the auxiliary compounds were taken from ref 40). This table shows that the theoretical estimates of the reaction enthalpies are in good agreement with the experimental values.

Earlier in this paper we mentioned conjugation as a mechanism for stabilization of 1-indanone but not for 2-indanone. We will now be somewhat more precise about this. The effect of conjugation can be evaluated as the difference of the gas phase enthalpies of formation of the two isomers as directly determined calorimetrically, alternatively recognized as the endothermicity of reaction 11. This difference is 7.4 ± 6.1 kJ mol^{-1}. Alternatively, we may consider the enthalpies of the isodesmic reactions 13 and 14. They are endothermic by 9.0 ± 6.4 and 1.6 ± 7.1 kJ mol^{-1}, respectively, the former entirely consistent with the above difference and conjugation enthalpy for the 1-indanone, and the latter entirely consistent with the absence of conjugation for the 2-isomer.

We recall that the oxidation potentials of a large collection of carbonyl (both aldehydes and ketones) compounds was reported nearly 60 years ago.[41] More precisely, the equilibrium constants of the reaction

$$\mathrm{RR^1CO + R^2R^3CHOH \rightarrow RR^1CHOH + R^2R^3CO} \qquad (16)$$

were determined and calibrated against the oxidation potentials for some thermochemically well-defined species. For 1- and 2-indanone the oxidation potentials were determined to be −14 and −27 kJ mol^{-1}. Consider the following plausible assumptions: solvent effects are assumed small and the difference between 1- and 2-indanone even smaller because these species are isomers. Electrochemical quantities such as these potentials directly relate to Gibbs energy through the Nernst equation, but let us assume the entropy effects are small. The entropy difference between 1- and 2-indanone are ever smaller. Gibbs energies can thus be equated to enthalpies in the current discussion. Lacking conjugation of the benzenoid ring with the nearby hydroxyl group, the reduction products 1- and 2-indanol are also assumed to have very similar enthalpies of formation and solvation effects. Ignoring any differences here, the difference in the enthalpies of formation of 1- and 2-indanone is deduced to be 13 kJ mol^{-1}. Our quantum chemical calculations at the highest level employed give a difference of 14.2 kJ mol^{-1}. It is seen that these diverse ways of deriving the conjugation energy of 1-indanone are entirely consistent. We suggest a consensus value of 11 ± 3 kJ mol^{-1}. (This value is also consistent with the consensus value of the conjugation energy of monocyclic enones of 13 ± 4 kJ suggested in ref 35, and with 15.4 ± 3.2 kJ mol^{-1} suggested for the isomeric cyclopentenones[12]).

Reaction 12 is found to be endothermic by 23.7 ± 6.9 kJ mol^{-1} from experimentally measured enthalpies of formation; the highest level theory results in a consistent value of 18.9 kJ mol^{-1}. We recognize this endothermicity as arising from multiple sources: (1) the presence of two electron withdrawing groups on the same benzene ring, additionally ortho such as in dimethyl phthalate (as opposed to its iso- and tere-phthalate isomers),[42] (2) the likewise vicinal and (*Z*)-situated groups in dimethyl maleate (as opposed to its fumarate isomer)[43] that are also conformationally rigid and have two carbonyl groups located β (1,3-) in an aliphatic chain[38] (note the new value of the enthalpy of formation of the archetypical β-diketone, "acetylacetone" in both its diketo and more stable enol forms, see ref 20), thereby having two positively charged carbons near each other resulting in electrostatic repulsion between them. Reactions 13 and 14 document the effect of affixing a benzene ring to a cyclopentanone. Although loss of conjugation for 1-indanone in reaction 13 is seen to be destabilizing, endothermicities of 9.0 ± 6.4 and 7.2 kJ mol^{-1} are found from experiment and from the highest level of calculational theory, the comparable reaction 14 for the nonconjugated 2-indanone is thermoneutral, the corresponding values being 1.6 ± 7.1 and −7.0 kJ mol^{-1}, respectively. Acknowledging the error bars in the measurements, computational theory and calorimetric experiment are in good accord for the first reaction and in acceptable agreement for the second. Reaction 15 combines both the stabilizing and destabilizing features mentioned above in a single reaction. Again, good agreement is found between calorimetric experiments and calculational theory, −5.7 ± 8.5 and −4.5 kJ mol^{-1}, respectively.

Conclusions

Through a composite of calorimetric and vapor pressure measurements, density functional calculations, and qualitative insights, we affirm that 1-indanone is conjugatively stabilized but its 2-isomer lacks such stabilization. 1,3-Indandione is destabilized compared to the corresponding monoketone because of the proximity and orientation of its two C═O groups.

Acknowledgment. We thank Profs. Dale L. Whalen and Ralph M. Pollack for numerous discussions on the energetics of cyclic ketones and related species.

Supporting Information Available: Experimental details including retention times, gas chromatographic correlation data, vaporization enthalpies, combustion energies, geometrical parameters, and energies, figures of atom numbering schemes, and references to literature data used. This material is available free of charge via the Internet at http://pubs.acs.org.

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