

# Calorimetric and Computational Study of Indanones

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

*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, University of Missouri—St. Louis, St. Louis, Missouri 63121, and Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, Maryland 21250*

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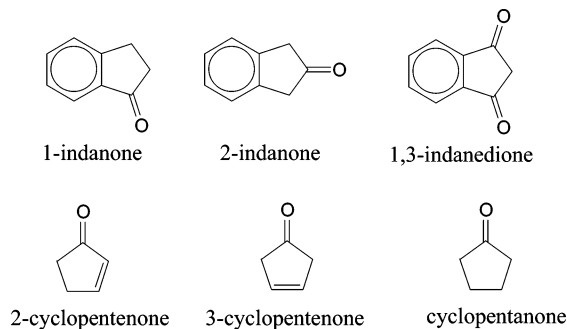
Condensed phase standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation for 1-indanone, 2-indanone, and 1,3-indandione were derived from the standard molar enthalpies of combustion, in oxygen, at  $T = 298.15$  K, measured by static bomb combustion calorimetry. The standard molar enthalpies of 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,  $-64.0 \pm 3.8$  kJ mol<sup>-1</sup>; 2-indanone,  $-56.6 \pm 4.8$  kJ mol<sup>-1</sup>; 1,3-indandione,  $-165.0 \pm 2.6$  kJ mol<sup>-1</sup>. 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.<sup>1</sup> The study of the acidity of 2-indanone provided seminal information as to the effects of phenyl groups on the acidification of ketones,<sup>2</sup> and thereby led to insights into the physical bioorganic chemistry of unsaturated ketones, in particular steroids such as testosterone.<sup>3</sup> 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.<sup>4</sup> Despite these enunciated applications, there has been little work reported regarding the structure and energetics of carbonyl-containing indene compounds.

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

## SCHEME 1: Structures of the Compounds Studied



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.<sup>5</sup> 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

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

<sup>†</sup> Centro de Investigação em Química, Departamento de Química, Faculdade de Ciências, Universidade do Porto.

<sup>‡</sup> ICBAS, Universidade do Porto.

<sup>||</sup> University of Missouri—St. Louis.

<sup>§</sup> University of Maryland.

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.<sup>6</sup> 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  $1.67 \times 10^{-2} \text{ K s}^{-1}$ . No phase transitions were observed between  $T = 298.15 \text{ K}$  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:<sup>7</sup> 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,  $100.00 \pm 0.03$ , 2-indanone,  $100.04 \pm 0.03$ , and 1,3-indandione,  $100.00 \pm 0.02$ . The specific densities of the samples were taken from ref 8 as  $\rho = 1.103 \text{ g cm}^{-3}$  (1-indanone),  $\rho = 1.0712 \text{ g cm}^{-3}$  (2-indanone), and  $\rho = 1.37 \text{ g cm}^{-3}$  (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,<sup>9,10</sup> 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  $\Delta_c u = -26435.1 \pm 3.5 \text{ J g}^{-1}$ , under certificate conditions. Calibration experiments were carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 cm<sup>3</sup> 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:  $\epsilon_{\text{cal}} = 16005.0 \pm 2.0 \text{ J K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean.

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

The electrical energy for ignition  $\Delta U(\text{ign})$  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  $\text{CH}_{1.686}\text{O}_{0.843}$ , the specific energy of combustion is  $\Delta_c u^\circ = -16240 \text{ J g}^{-1}$ ,<sup>11</sup> a value previously confirmed in our laboratory. The corrections for nitric acid formation  $\Delta U(\text{HNO}_3)$  were based on  $-59.7 \text{ kJ mol}^{-1}$ ,<sup>12</sup> for the molar energy of formation of 0.1 mol dm<sup>-3</sup>  $\text{HNO}_3(\text{aq})$  from  $\text{N}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{l})$ . 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,<sup>13</sup> who determined the specific energy of combustion of dry Melinex as  $\Delta_c u^\circ = -22902 \pm 5 \text{ J g}^{-1}$ . 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.<sup>13</sup> 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  $\Delta_c u^\circ = -47160.8 \pm 4.1 \text{ J g}^{-1}$ .

The mass of compound,  $m(\text{compound})$ , used in each experiment was determined from the total mass of carbon dioxide,  $m(\text{CO}_2, \text{total})$ , produced after allowance for that formed from the cotton thread fuse, Melinex and *n*-hexadecane.

An estimated pressure coefficient of specific energy:  $(\partial u / \partial p)_T = -0.2 \text{ J g}^{-1} \text{ MPa}^{-1}$  at  $T = 298.15 \text{ K}$ , a typical value for most organic compounds, was assumed.<sup>14</sup> 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.<sup>15</sup>

### Calvet Microcalorimetry Experiments

The standard molar enthalpies of sublimation were measured using the “vacuum sublimation” drop microcalorimetric method,<sup>16</sup> 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  $72.600 \pm 0.600 \text{ kJ mol}^{-1}$ .<sup>17</sup> Accuracy tests were performed with benzoic acid.

The observed enthalpies of sublimation,  $\Delta_{\text{cr}, 298.15 \text{ K}}^{\text{g}, T} H_m^\circ$ , were corrected to  $T = 298.15 \text{ K}$  using the equation

$$\Delta_{298.15 \text{ K}}^T H_m^\circ(\text{g}) = \int_{298.15 \text{ K}}^T C_{p, \text{m}}^\circ(\text{g}) dT \quad (1)$$

where  $T$  is the temperature of the hot reaction vessel and  $C_{p, \text{m}}^\circ(\text{g})$  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,

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

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

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

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,<sup>17</sup> the coefficients for  $(T/\text{K})^2$ ,  $(T/\text{K})$ , 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.<sup>18</sup>

### 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**

$T/\text{K}$	$p/\text{Pa}$	$\Delta p/\text{Pa}^a$
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

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

vaporization.<sup>19</sup> The uncertainty in the pressure measurements is adequately described by the equation  $\sigma(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$ , 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,  $\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^0$ ,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0$ , and  $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^0$ , were derived by fitting the Clarke and Glew equation (eq 5) to the vapor pressure results presented in Table 1.

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

In this equation,  $p$  is the vapor pressure at the temperature  $T$ ,  $p^0$  is a selected reference pressure (in this work we took  $p^0 = 10^5$  Pa),  $\theta$  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<sup>-1</sup> mol<sup>-1</sup>), and  $\Delta_{\text{cr}}^{\text{g}} G_{\text{m}}^0$ ,  $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0$ , and  $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^0$  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,<sup>19</sup> 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  $\Omega$ ; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be less than  $\pm 0.01$  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,<sup>20</sup> 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,  $t_{\text{a}}$ . The quantity  $t_{\text{a}}$  is inversely proportional to the compounds vapor pressure. A plot of  $\ln(t_{\text{o}}/t_{\text{a}})$  against  $1/T$  (K<sup>-1</sup>), where  $t_{\text{o}}$  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,  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}(T_{\text{m}})$ , is a sum of the vaporization enthalpy of the analyte and its enthalpy of interaction with the column at the mean temperature of measurement,  $T_{\text{m}}$ . Provided the structure of the reference materials are properly selected,  $\Delta_{\text{sln}}^{\text{g}} H_{\text{m}}(T_{\text{m}})$  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.

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

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

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

### Computational Details

The geometries of the compounds studied were fully optimized using density functional theory (DFT) with the Becke three-parameter hybrid exchange<sup>22</sup> and Lee–Yang–Parr<sup>23</sup> correlation density functional (B3LYP) and two different basis sets: 6-31G\*<sup>24</sup> and 6-311G\*\*.<sup>25</sup> 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 energies were also obtained from single-point calculations at the most stable B3LYP/6-311G\*\* geometries, using the triple- $\zeta$  correlation consistent basis set, cc-pVTZ,<sup>26</sup> and also with the MPW1B95<sup>27</sup> density functional using the 6-311G\*\* and cc-pVTZ basis sets. All calculations were performed using the UK

**TABLE 2: Summary of the DSC Results**

compound	$\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(T_{\text{fus}})/$ (kJ mol <sup>-1</sup> )	$T_{\text{fus}}/K$	$C_p(l)^c/$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_p(\text{cr})^c/$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta_{\text{cr}}^1 H_{\text{m}}^{\circ}(298.15 \text{ K})/$ (kJ mol <sup>-1</sup> ) <sup>d</sup>	mol %
1-indanone	17.6 ± 0.22 17.8 <sup>a</sup>	314.14 ± 0.04 312.9 <sup>a</sup>	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 <sup>b</sup>	401.5	236.5	180.2	17.2	decomposes on fusion

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

265 version of GAMESS,<sup>28,29</sup> except the calculations with the density  
266 functional MPW1B95, which were performed with the Gaussian  
267 03 series of programs.<sup>30</sup>

## 268 Experimental Results

269 **DSC Results.** The purity of the compounds was assessed  
270 using differential scanning calorimetry (DSC) except for 1,3-  
271 indandione, which decomposes slightly during the fusion  
272 process. The temperatures (observed at the onset of the  
273 calorimetric peaks) and enthalpies of fusion and the molar  
274 fractions of purity were computed from the DSC thermo-  
275 grams: The DSC results are summarized in Table 2. The  
276 uncertainties assigned to the results are twice the standard  
277 deviation of the mean of five independent runs.

278 Some decomposition of 1,3-indandione was indicated by the  
279 fact that upon cooling and reheating, both the enthalpy and peak  
280 shape deteriorated slightly. Though most organic compounds  
281 show slightly smaller fusion enthalpies upon reheating, continu-  
282 ous recycling clearly indicated decomposition. Slight decom-  
283 position is also indicated by the sublimation enthalpy calculated  
284 from the sum of the vaporization and fusion enthalpies discussed  
285 below.

286 Fusion enthalpies were adjusted to  $T = 298.15$  K using the  
287 following equation:<sup>31</sup>

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

288 Heat capacities of the solid,  $C_p(\text{cr})$ , and liquid phase,  $C_p(l)$ , were  
289 estimated and an uncertainty of one-third of the temperature  
290 adjustment was arbitrarily assigned.

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

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

295 where  $\Delta U(\text{IBP})$  is the energy associated with the isothermal  
296 bomb process,  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water  
297 added to the calorimeter from 3119.6 g,  $c_p(\text{H}_2\text{O}, l)$  is the specific  
298 heat capacity of liquid water,  $\epsilon_f$  is the energy of the bomb  
299 contents after ignition,  $\Delta T_{\text{ad}}$  is the adiabatic temperature increase  
300 raise calculated using the program LABTERMO,<sup>32</sup> and  $\Delta U_{\text{ign}}$   
301 is the energy of ignition.

302 The individual results of the massic energies of combustion,  
303  $\Delta_{\text{c}}u^{\circ}$ , at  $T = 298.15$  K, of all combustion experiments, together  
304 with the mean value and its standard deviation, are given for  
305 each compound in Table S8 of Supporting Information. Table  
306 4 lists the derived standard molar energies and enthalpies of  
307 combustion,  $\Delta_{\text{c}}U_{\text{m}}^{\circ}(\text{cr})$  and  $\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{cr})$ , and the standard molar  
308 enthalpies of formation of the compounds in the crystalline  
309 phase,  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ , at  $T = 298.15$  K. In accordance with

**TABLE 3: Typical Combustion Experiments at  $T = 298.15$  K<sup>a</sup>**

	1-indanone	2-indanone	1,3-indandione
$m(\text{CO}_2, \text{total})/\text{g}$	2.05575	1.81146	2.30867
$m(\text{compound})/\text{g}$	0.64130	0.56385	0.61578
$m(\text{fuse})/\text{g}$	0.00216	0.00223	0.00214
$m(n\text{-hexadecane})/\text{g}$			0.20462
$m(\text{Melinex})/\text{g}$	0.05689	0.05153	
$\Delta T_{\text{ad}}/K$	1.45961	1.28760	1.69364
$\epsilon_f/(J \text{ K}^{-1})$	16.29	15.82	16.85
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0
$-\Delta U(\text{IBP})/J$	23383.65	20627.21	27134.06
$\Delta U(\text{fuse})/J$	35.08	36.22	34.75
$\Delta U(n\text{-hexadecane})/J$			9650.20
$\Delta U(\text{Melinex})/J$	1302.84	1180.16	
$\Delta U(\text{HNO}_3)/J$	6.87	3.56	0.24
$\Delta U(\text{carbon})/J$	0.00	0.00	0.00
$\Delta U(\text{ign.})/J$	1.19	1.20	1.19
$\Delta U_{\Sigma}/J$	14.35	12.43	15.84
$-\Delta_{\text{c}}u^{\circ}/(J \text{ g}^{-1})$	34343.54	34397.16	28310.48

<sup>a</sup>  $m(\text{CO}_2, \text{total})$  is the total mass of  $\text{CO}_2$  formed in the experiment;  $m(\text{compound})$  is the mass of compound burnt in the experiment;  $m(\text{fuse})$  is the mass of fuse (cotton) used in the experiment;  $m(n\text{-hexadecane})$  is the mass of  $n$ -hexadecane used in the experiment;  $m(\text{Melinex})$  is the mass of Melinex used in the experiment;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\epsilon_f$  is the energy equivalent of contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of the mass of water added to the calorimeter from 3119.6 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{IBP})$  includes the ignition energy,  $\Delta U(\text{ignition})$ ;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta U(n\text{-hexadecane})$  is the energy of combustion of  $n$ -hexadecane;  $\Delta U(\text{Melinex})$  is the energy of combustion of Melinex;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{carbon})$  is the energy correction for carbon formation;  $\Delta U_{\Sigma}$  is the energy correction to the standard state;  $\Delta_{\text{c}}u^{\circ}$  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<sup>-1</sup>)**

compound	$\Delta_{\text{c}}U_{\text{m}}^{\circ}(\text{cr})$	$\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{cr})$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$
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

310 customary thermochemical practice,<sup>33,34</sup> the uncertainties as-  
311 signed to the standard molar enthalpies of combustion are, in  
312 each case, twice the overall standard deviation of the mean and  
313 include the uncertainties in calibration and in the values of the  
314 auxiliary quantities used. To derive  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$  from  $\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{cr})$   
315 the standard molar enthalpies of formation of  $\text{H}_2\text{O}(l)$  and  $\text{CO}_2$ -  
316 (g), at  $T = 298.15$  K, were taken, respectively as,  $-285.830 \pm$   
317  $0.042$  kJ mol<sup>-1</sup><sup>33</sup> and  $-393.51 \pm 0.13$  kJ mol<sup>-1</sup>.<sup>33</sup>

318 **Calvet Microcalorimetry, Correlation-Gas Chromatog-**  
319 **raphy, and Vapor Pressure Results.** The standard molar  
320 enthalpies of sublimation of the three indanones were measured  
321 by Calvet microcalorimetry. The experimental results are given  
322 in Table 5 for the three compounds with uncertainties of twice  
323 the standard deviation of the mean. For 1- and 2-indanone the

**TABLE 5: Calorimetric Standard ( $p^\circ = 0.1$  MPa) Molar Enthalpies of Sublimation, at  $T = 298.15$  K (kJ mol<sup>-1</sup>)**

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

**TABLE 6: Summary of Fusion, Vaporization, and Sublimation Enthalpies by Correlation-Gas Chromatography (kJ mol<sup>-1</sup>)**

compound	$\Delta_{\text{cr}}^{\text{l}}H_m^\circ(298)$	$\Delta_{\text{f}}^{\text{g}}H_m^\circ(298)$	$\Delta_{\text{f}}^{\text{g}}H_m^\circ(298)$
1-indanone	$17.0 \pm 0.2$	$60.4 \pm 2.8$	$77.4 \pm 2.8$
2-indanone	$15.6 \pm 0.4$	$58.9 \pm 2.8$	$74.5 \pm 2.8$
1,3-indandione	$17.2^a$	$72.6 \pm 2.0$	89.8

<sup>a</sup> This result for 1,3-indandione assumes the material is stable at its fusion temperature.

**TABLE 7: Derived Standard ( $p^\circ = 0.1$  MPa) Molar Values of the Enthalpies of Formation in the Gas Phase, at  $T = 298.15$  K (kJ mol<sup>-1</sup>)**

compound	$\Delta_{\text{f}}H_m^\circ(\text{cr})$	$\Delta_{\text{cr}}^{\text{g}}H_m^\circ$	$\Delta_{\text{f}}H_m^\circ(\text{g})$
1-indanone	$-142.0 \pm 2.6$	$78.0 \pm 1.3$	$-64.0 \pm 3.8$
2-indanone	$-133.0 \pm 2.9$	$76.4 \pm 3.8$	$-56.6 \pm 4.8$
1,3-indandione	$-260.0 \pm 2.5$	$95.0 \pm 0.7$	$-165.0 \pm 2.6$

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  $\Delta_{\text{cr}}^{\text{g}}G_m^\circ/(\text{J mol}^{-1}) = 36095 \pm 40$ ,  $\Delta_{\text{cr}}^{\text{g}}H_m^\circ/(\text{kJ mol}^{-1}) = 95.0 \pm 0.7$ , and  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1}) = -93 \pm 16$ . 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  $22.4 \pm 2.0$  kJ mol<sup>-1</sup> 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<sup>21</sup> reported the standard enthalpies of formation in the crystalline and gaseous phases, respectively, of  $-145.25 \pm 0.87$  kJ mol<sup>-1</sup> and  $-61.7 \pm 1.1$  kJ mol<sup>-1</sup>, using a standard enthalpy of sublimation of  $83.51 \pm 0.73$  kJ mol<sup>-1</sup>. 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;<sup>1</sup> a planar structure was also found. Among the most telling geometric parameters are the considerably shorter “C sp<sup>2</sup>-CO” bonds in 1-indanone, 1,3-indandione, and 2-cyclopentenone, than the “C sp<sup>3</sup>-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<sup>1</sup> and for 1,3-indandione.<sup>35</sup> The calculated geometrical parameters are in generally good agreement with the experimental values.

Autrey and Laane<sup>36</sup> 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<sub>2</sub>-CH<sub>2</sub> torsional interactions. 2-Cyclopentenone does have such a CH<sub>2</sub>-CH<sub>2</sub> 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<sup>37</sup> and by direct isomer equilibration.<sup>38</sup> Hence, 2-cyclopentenone is also planar. A similar explanation is 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

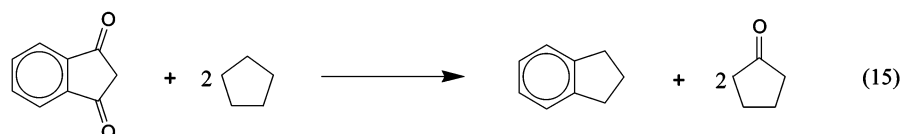
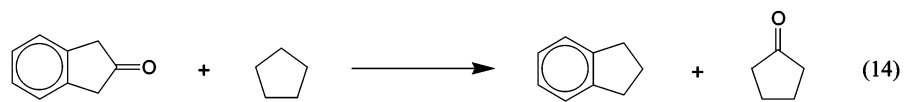
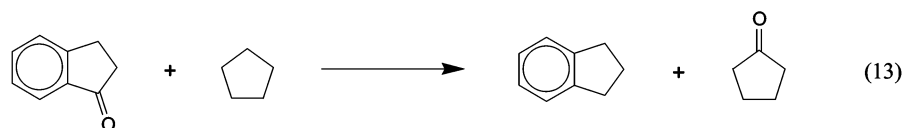
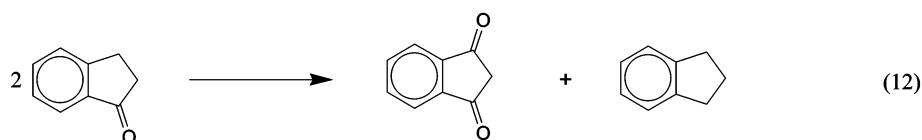
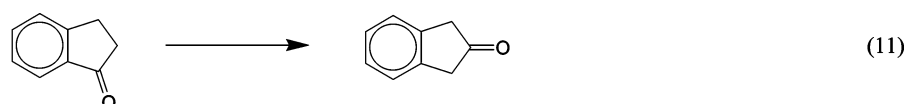
**TABLE 8: Calculated Reaction Energies at  $T = 0$  K and Enthalpies at  $T = 298.15$  K (kJ mol<sup>-1</sup>)**

reaction	$\Delta_r E_T = 0\text{ K}$				$\Delta_r H_T^\circ = 298.15\text{ K}$				
	B3LYP		MPW1B95		B3LYP		MPW1B95		exp <sup>a</sup>
	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	6-311G**	cc-pVTZ	
11	17.1	16.5	15.6	15.3	14.8	14.2	13.3	13.1	$7.4 \pm 6.1$
12	18.8	19.6	18.0	18.6	18.2	18.9	17.4	18.0	$23.7 \pm 6.9$
13	10.4	9.2	6.9	6.2	8.5	7.2	5.0	4.3	$9.0 \pm 6.4$
14	-6.7	-7.3	-8.6	-9.1	-6.4	-7.0	-8.3	-8.8	$1.6 \pm 7.1$
15	2.1	-1.2	-4.1	-6.1	-1.2	-4.5	-7.3	-9.4	$-5.7 \pm 8.5$

<sup>a</sup> The experimental values of the enthalpies of formation of auxiliary molecules were taken from ref 40.

399 B3LYP/6-311G\*\* geometries, and also with the MPW1B95  
400 functional using the 6-311G\*\* and the cc-pVTZ basis sets. The  
401 resulting electronic energies are shown in Table S11 under the  
402 appropriate headings, as well as the thermal corrections to  $T =$   
403 298.15 K. In this table we also show the corresponding energies  
404 of some auxiliary molecules. Comparison of our experimental  
405 enthalpies of formation in the gaseous phase and the theoretical  
406 calculations for the two isomeric indanones shows that 1-in-  
407 danone is energetically more stable than the 2-isomer. This  
408 presumably arises from the conjugation between the C=O and  
409 the benzenoid ring in the 1-indanone isomer, a stabilizing  
410 mechanism absent in the 2-indanone isomer.<sup>39</sup>

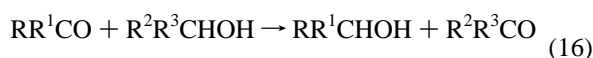
411 To evaluate the accuracy of the calculations, we have  
412 considered the following isodesmic reactions:



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

420 Earlier in this paper we mentioned conjugation as a mech-  
421 anism for stabilization of 1-indanone but not for 2-indanone.  
422 We will now be somewhat more precise about this. The effect  
423 of conjugation can be evaluated as the difference of the gas  
424 phase enthalpies of formation of the two isomers as directly  
425 determined calorimetrically, alternatively recognized as the  
426 exothermicity of reaction 11. This difference is  $7.4 \pm 6.1$  kJ  
427 mol<sup>-1</sup>. Alternatively, we may consider the enthalpies of the  
428 isodesmic reactions 13 and 14. They are endothermic by  $9.0 \pm$   
429  $6.4$  and  $1.6 \pm 7.1$  kJ mol<sup>-1</sup>, respectively, the former entirely  
430 consistent with the above difference and conjugation enthalpy  
431 for the 1-indanone, and the latter entirely consistent with the  
432 absence of conjugation for the 2-isomer.

433 We recall that the oxidation potentials of a large collection  
434 of carbonyl (both aldehydes and ketones) compounds was  
435 reported nearly 60 years ago.<sup>41</sup> More precisely, the equilibrium  
436 constants of the reaction



437 were determined and calibrated against the oxidation potentials  
438 for some thermochemically well-defined species. For 1- and  
439 2-indanone the oxidation potentials were determined to be  $-14$   
440 and  $-27$  kJ mol<sup>-1</sup>. Consider the following plausible assump-  
441 tions: solvent effects are assumed small and the difference  
442 between 1- and 2-indanone even smaller because these species  
443 are isomers. Electrochemical quantities such as these potentials  
444 directly relate to Gibbs energy through the Nernst equation, but  
445 let us assume the entropy effects are small. The entropy  
446 difference between 1- and 2-indanone are ever smaller. Gibbs  
447 energies can thus be equated to enthalpies in the current

448 discussion. Lacking conjugation of the benzenoid ring with the  
449 nearby hydroxyl group, the reduction products 1- and 2-indanol  
450 are also assumed to have very similar enthalpies of formation  
451 and solvation effects. Ignoring any differences here, the differ-  
452 ence in the enthalpies of formation of 1- and 2-indanone is  
453 deduced to be 13 kJ mol<sup>-1</sup>. Our quantum chemical calculations  
454 at the highest level employed give a difference of 14.2 kJ mol<sup>-1</sup>.  
455 It is seen that these diverse ways of deriving the conjugation  
456 energy of 1-indanone are entirely consistent. We suggest a  
457 consensus value of  $11 \pm 3$  kJ mol<sup>-1</sup>. (This value is also  
458 consistent with the consensus value of the conjugation energy  
459 of monocyclic enones of  $13 \pm 4$  kJ suggested in ref 35, and  
460 with  $15.4 \pm 3.2$  kJ mol<sup>-1</sup> suggested for the isomeric cyclopent-  
461 enones<sup>12</sup>).

462 Reaction 12 is found to be endothermic by  $23.7 \pm 6.9$  kJ  
463 mol<sup>-1</sup> from experimentally measured enthalpies of formation;  
464 the highest level theory results in a consistent value of 18.9 kJ  
465 mol<sup>-1</sup>. We recognize this endothermicity as arising from  
466 multiple sources: (1) the presence of two electron withdrawing  
467 groups on the same benzene ring, additionally ortho such as in  
468 dimethyl phthalate (as opposed to its iso- and tere-phthalate  
469 isomers),<sup>42</sup> (2) the likewise vicinal and (*Z*)-situated groups in  
470 dimethyl maleate (as opposed to its fumarate isomer)<sup>43</sup> that are  
471 also conformationally rigid and have two carbonyl groups  
472 located  $\beta$  (1,3-) in an aliphatic chain<sup>38</sup> (for a new value of the  
473 enthalpy of formation of the archetypal  $\beta$ -diketone, "acety-

474 acetone" in both its diketo and more stable enol forms, see ref  
475 20), thereby having two positively charged carbons near each  
476 other resulting in electrostatic repulsion between them. Reactions  
477 13 and 14 document the effect of affixing a benzene ring to a  
478 cyclopentanone. Although loss of conjugation for 1-indanone  
479 in reaction 13 is seen to be destabilizing, endothermicities of  
480  $9.0 \pm 6.4$  and  $7.2 \text{ kJ mol}^{-1}$  are found from experiment and  
481 from the highest level of calculational theory, the comparable  
482 reaction 14 for the nonconjugated 2-indanone is thermoneutral,  
483 the corresponding values being  $1.6 \pm 7.1$  and  $-7.0 \text{ kJ mol}^{-1}$ ,  
484 respectively. Acknowledging the error bars in the measurements,  
485 computational theory and calorimetric experiment are in good  
486 accord for the first reaction and in acceptable agreement for  
487 the second. Reaction 15 combines both the stabilizing and  
488 destabilizing features mentioned above in a single reaction.  
489 Again, good agreement is found between calorimetric experi-  
490 ments and calculational theory,  $-5.7 \pm 8.5$  and  $-4.5 \text{ kJ mol}^{-1}$ ,  
491 respectively.

## 492 Conclusions

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

499 **Supporting Information Available:** Experimental details  
500 including retention times, gas chromatographic correlation data,  
501 vaporization enthalpies, combustion energies, geometrical pa-  
502 rameters, and energies, figures of atom numbering schemes, and  
503 references to literature data used. This material is available free  
504 of charge via the Internet at <http://pubs.acs.org>.

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564 H. de Vries. The package is derived from the original GAMESS code due  
565 to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog,  
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