Thermochemical and Crystallographic Studies of some β-Ketoimine Derivatives

Manuel A. V. Ribeiro Da Silva,[a] Maria D. M. C. Ribeiro Da Silva,[a] José P. A. Paiva,[a] Isabel M. C. S. Nogueira,[a] A. Margarida Damas,[d] James V. Barkley,[b] Marjorie M. Harding,[b] Margaret J. Akello[c] and Geoffrey Pilcher[c]
[a] *Centro de Investigação em Química, Faculdade de Ciências, Universidade do Porto, P-4000 Porto, Portugal*
[b] *Department of Chemistry, University of Liverpool, PO Box 147, Liverpool UK L69 3BX*
[c] *Department of Chemistry, University of Manchester, Manchester UK M13 9PL*
[d] *Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, Largo do Prof. Abel Salazar, No. 2, P-4000, Porto, Portugal*

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation at 298.15 K in the gaseous state of some β-ketoimines, $RCOCH{=}C(CH_3)NHR^1$, were determined from their enthalpies of combustion and of sublimation, $\Delta_fH^\circ_m(g)/kJ\ mol^{-1}$: $R{=}CH_3$, $\{R^1 = C_6H_5, -66.0 \pm 4.2; R^1 = p\text{-}C_6H_4NO_2, -98.9 \pm 5.0\}$: $R = C_6H_5$, $\{R^1 = H, -48.7 \pm 3.5; R^1 = CH_3, -53.7 \pm 4.7; R^1 = C_6H_5, 69.1 \pm 4.2\}$. From these results it is shown that the increase in delocalization energy from $R = CH_3$ to $R = C_6H_5$ matches the corresponding increase between acetylacetone and benzoylacetone. Crystal structures are reported for $R = CH_3$, $R^1 = p\text{-}C_6H_4NO_2$, and $R = C_6H_5$ $\{R^1 = H, R^1 = CH_3\}$, and show that those β-ketoimines with $R = C_6H_5$ have a more delocalized structure in the $-COCH{=}C(CH_3)NH-$moiety than those with $R = CH_3$ in accord with the thermochemical results.

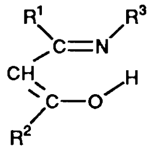
The thermochemistry of β-diketones and of their metal chelate complexes has been extensively studied and reviewed,[1] but the properties of β-ketoimines, Schiff base derivatives of the β-diketones and the corresponding metal chelate complexes have received much less attention.

Three forms, **I**, **II** and **III** may be considered for the basic structure of a β-ketoimine. Ueno and Martell,[2] from IR spectra concluded that a tautomeric equilibrium exists between forms **I** and **II**, and that form **III** can be excluded because no absorption was observed in the region of 1700 cm^{-1}, typical of a free carbonyl group. Cromwell *et al.*[3] from IR spectra presented convincing evidence that form **II** was dominant. Martin *et al.*[4] however, from a study of the acid dissociation constants in aqueous dioxan, concluded that form **I** is of major importance in solution. Both structures **I** and **II** will exhibit delocalization and the extent may be influenced by the nature of the groups, R^1, R^2 and R^3.

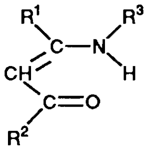
For the metal chelate complexes of β-ketoimines, some stability constants have been measured,[4] IR spectra reported,[5] but only a single thermochemical result, the enthalpy of formation of bis(4-phenylaminopent-3-ene-2-one) copper (II),[6] is known.

The present paper reports the standard molar enthalpies of formation of five crystalline β-ketoimines, determined by static-bomb combustion calorimetry and the standard molar enthalpies of sublimation measured by microcalorimetry; from these results the standard molar enthalpies of formation in the gaseous state were derived. Crystal structures by X-ray analysis were determined for the β-ketoimines, **2**, **3** and **4**; they show that in the crystalline state tautomer **II** is present and comparisons of the bond lengths provide information on changes in the extent of delocalization in these derivatives.

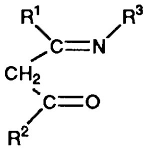
$RCOCH{=}C(CH_3)NHR^1$
$R = CH_3, R^1 = C_6H_5$ (**1**)
$R = CH_3, R^1 = p\text{-}C_6H_4NO_2$ (**2**)
$R = C_6H_5, R^1 = H$ (**3**)
$R = C_6H_5, R^1 = CH_3$ (**4**)
$R = R^1 = C_6H_5$ (**5**)



I



II



III

Experimental

Materials.—4-Phenylaminopent-3-ene-2-one (**1**) was prepared as described by Roberts and Turner,[7] aniline plus pentane-2,4-dione were refluxed for 2 h, followed by refluxing with water. The compound was extracted with benzene, dried (anhyd. sodium sulfate) and the benzene removed by evaporation. The product was filtered, dried and purified by repeated sublimation *in vacuo*. 4-*p*-Nitrophenylpent-3-ene-2-one (**2**) was prepared as described by Martin *et al.*;[4] *p*-nitroaniline and an excess of pentane-2,4-dione with 2 drops of sulfuric acid were refluxed in benzene, water was removed as it was formed. The product crystallized on cooling and was recrystallized twice from a mixture of benzene and light petroleum (1 : 1 v) to yield monoclinic plates. 3-Amino-1-phenyl-but-2-enone (**3**) was prepared by the method of Holtzclaw *et al.*[5] Aqueous ammonia (25%) was refluxed with 1-phenyl-butane-1,3-dione for 3 h. The sample precipitated on cooling and for the combustion measurements was purified by repeated sublimation *in vacuo*. For X-ray analysis, crystals were grown from a solution in diethyl ether to produce orthorhombic prisms. The compound was characterized by elemental analysis and the IR spectrum. 3-Methylamino-1-phenyl-but-2-enone (**4**) was prepared in a manner similar to that for **3** except that a solution of methylamine in ethanol (33%) was used. The product was purified by twice recrystallizing from diethyl ether to yield orthorhombic prisms. 3-Anilino-1-phenylbut-2-enone (**5**) was prepared by the method of Martin *et al.*,[4] by condensation of equimolar quantities of aniline and benzoylacetone. The sample was purified by recrystallizing three times from ethanol.

The average ratios of the mass of carbon dioxide produced from the sample in the combustion experiments to that calculated from its mass with uncertainties of twice the standard deviation of the mean were: **3**, 0.9997 ± 0.0001; **4**, 0.9995 ± 0.0002; **5**, 0.9997 ± 0.0002; **1**, 1.0001 ± 0.0002; **2**, 1.0000 ± 0.0002.

Combustion Calorimetry.—The energy of combustion of **1** was measured using the static-bomb calorimeter in Manchester,[8] the other compounds were measured using the static-bomb calorimeter in Porto.[9,10] The energy equivalent of the Manchester bomb calorimeter was determined using the combustion of benzoic acid, NBS SRM 39i, having a specific energy of combustion under standard bomb conditions of 26434 ± 3 J g^{-1}: from eight calibrations, ε(calor) = 15302.70 ± 0.77 J K^{-1}, where the uncertainty is the standard deviation of the mean, for an average mass of water added to the calorimeter of 2897.0 g. The Porto bomb calorimeter was calibrated using B.D.H. Thermochemical Standard Benzoic Acid for which under standard bomb conditions, $-\Delta_c u$ = 26434.9 ± 3.7 J g^{-1}. During these measurements several changes were made to the calorimeter resulting in changes to ε(calor): for **3**, from seven calibrations ε(calor) = 16017.2 ± 1.7 J K^{-1}; for **4** and **5**, from five calibrations ε(calor) = 16016.7 ± 0.4 J K^{-1}; and for **2**, from nine calibrations ε(calor) = 16000.2 ± 1.7 J K^{-1}. In all cases ε(calor) was corrected for an average mass of water of 3119.6 g added to the calorimeter.

Although different bomb calorimeters were used, many of the experimental conditions were the same. The samples, in pellet form, 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 for 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 $CH_{1.686}O_{0.843}$, $-\Delta_c u^0$ = 16250 J g^{-1}.[11] 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).[12] For **3**, hexadecane (Aldrich Gold Label, stored under nitrogen) was required as an auxiliary combustion aid: from separate experiments, $-\Delta_c u^0$(hexadecane) = 47147.4 ± 5.9 J g^{-1}. For each compound $(\delta u/\delta p)_T$ at 298.15 K was assumed to be −0.1 J g^{-1} MPa^{-1}, a value typical for organic solids. 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 and hexadecane auxiliary. $\Delta_c u^0$ for each compound was calculated by the procedure given by Hubbard *et al.*[11] The relative atomic masses used were those recommended by the IUPAC Commission.[13]

Enthalpies of Sublimation.—The standard molar enthalpies of sublimation were measured by the 'vacuum sublimation' drop microcalorimetric method.[14] Samples, about 5 mg, of each compound contained in a thin small glass capillary tube sealed at one end were dropped at room temp. into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter held at a constant temperature between 360 K and 420 K, and then removed from the hot-zone by vacuum sublimation. The observed molar enthalpies of sublimation $\{H^o_m(g,T) - H^o_m(cr, 298.15\ K)\}$ were corrected to 298.15 K using $\Delta^T_{298.15\ K}H^o_m(g)$ estimated by a group method based on the data of Stull *et al.*[15] The microcalorimeter was calibrated *in situ* for these measurements by making use of the reported enthalpy of sublimation of naphthalene, 72.51 ± 0.01 kJ mol^{-1}.[16]

Crystal Structure.—*Crystal data*. **3**: $C_{10}H_{11}NO$, M = 161.2. Orthorhombic, a = 19.893 (6), b = 9.874 (8), c = 8.760 (6) Å, V = 1721 Å^3, space group *Pbca* (by systematic absences), Z = 8, ρ_c = 1.245 g cm^{-3}. A clear prism with approximate dimensions of 0.40 × 0.15 × 0.40 mm was used for data collection. μ(Mo Kα) = 0.75 cm^{-1}.

4: $C_{11}H_{13}NO$, M = 175.2. Orthorhombic, a = 10.205 (3), b = 25.882 (6), c = 7.398 (4) Å, V = 1954 Å^3, space group *Pbca* (by systematic absences), Z = 8, ρ_c = 1.191 g cm^{-3}. A white prism crystal with approximate dimensions of 0.40 × 0.15 × 0.40 mm was used for data collection. μ(MoKα) = 0.71 cm^{-1}.

2: $C_{11}H_{12}N_2O_3$, M = 220.2. Monoclinic, a = 4.370 (3), b = 13.157 (3), c = 18.876 (2) Å, β = 93.24 (3) °, V = 1084 Å^3, space group $P2_1/n$ (by systematic absences), Z = 4, ρ_c = 1.350 g cm^{-3}. An orange plate crystal with approximate dimensions 0.45 × 0.15 × 0.75 mm was used for data collection. μ(Mo-Kα) = 0.93 cm^{-1}.

Data collection and processing. Measurements were made using a Rigaku AFC6S diffractometer with graphite monochromatized MoKα radiation. Cell constants were refined and data were collected using the ω–2θ scan technique to a maximum 2θ value of 50°. In each case the intensities of three representative reflections were measured after every 150 reflections and remained constant throughout data collection, hence no delay correction was required. The data were corrected for Lorentz and polarization effects. For **3**, 1784 unique reflections were collected, 2016 for **4** and 2006 for **2**.

The structures were solved by direct methods[17,18] and refined by least-squares.[19] Difference Fourier maps confirmed the presence of hydrogen atoms at the stereochemically expected positions and a preliminary refinement of their U values was performed; the non-hydrogen atoms were refined anisotropically. A weighting scheme dependent on both F(obs.) and $\sigma[F(\text{obs.})]$ was used.

For **3**, R converged to 0.055 (R_w = 0.049) for 684 reflections with $I > 3\sigma(I)$: for **4**, R = 0.052 (R$_w$ = 0.051) for 870 reflections with $I > 3\sigma(I)$; and for **2**, R = 0.045 (R_w = 0.045) for 1179 reflections with $I > 4\sigma(I)$. Maximum and minimum electron densities in final difference map were 0.18, −0.17 (**3**), 0.15, −0.19 (**4**), and 0.22, −0.20 eA^{-3} (**2**).

Results and Discussion

Thermochemical.—Results for a typical combustion experiment on each compound are given in Table 1; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from that assigned to ε(calor); ΔU_Σ is the correction to the standard state; the remaining terms are as previously defined.[11] As samples were ignited at 298.15 ± 0.001 K, $\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(H_2O,l)\Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} + \Delta U(\text{ign})$, where ΔT_{ad} is the calorimeter temperature change corrected for heat exchange and the work of stirring. The individual values of $\Delta_c u^o$ with the mean and its standard deviation are given in Table 2. Table 3 lists the derived standard molar enthalpies of combustion and formation where in accordance with normal thermochemical practice, the uncertainties assigned are twice the overall standard deviations of the means and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_f H^o_m$ from $\Delta_c H^o_m$ the standard molar enthalpies of formation for H_2O(l) (−285.83 ± 0.04 kJ mol^{-1}) and for CO_2(g) (− 393.51 ± 0.13 kJ mol^{-1}) were used.[20]

Crystal Structures.—Positional parameters have been deposited with CCDC,* the molecules are illustrated in Fig. 1 and

---

* For details of the Cambridge Crystallographic Data Centre deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Table 1 Typical combustion results ($p^\circ = 0.1$ MPa)

	1	**2**	**3**	**4**	**5**
$m(CO_2,\text{total})$/g	2.350 55	1.358 29	2.116 36	2.281 57	2.548 26
m(cpd.)/g	0.849 20	0.615 31	0.449 44	0.824 17	0.857 08
m(hexadecane)/g	—	—	0.284 24	—	—
m(fuse)/g	0.002 76	0.003 53	0.003 49	0.002 86	0.003 08
ΔT_{ad}/K	1.914 74	1.022 15	1.771 25	1.774 77	1.892 72
ε_f/J K^{-1}	14.0	15.3	16.8	16.5	16.8
$\Delta_m(H_2O)$/g	0.1	0.0	0.1	0.1	0.4
$-\Delta U$(IBP)/J	29 327.1	16 369.1	28 399.7	28 455.0	30 349.0
$\Delta U(HNO_3)$/J	71.5	38.8	27.3	43.0	24.1
ΔU(ign)/J	0.3	1.2	0.5	1.0	1.1
ΔU_Σ/J	16.0	11.2	12.8	16.0	18.5
$-m\Delta_c u^\circ$(fuse)/J	44.8	57.3	55.2	46.5	50.0
$-m\Delta_c u^\circ$(hexadecane)/J	—	—	13 403.6	—	—
$-\Delta_c u^\circ$(cpd.)/J g^{-1}	34 379.2	26 428.6	33 154.1	34 397.6	35 301.7

Table 2 Values of $-\Delta_c u^\circ$(J g^{-1}) at 298.15 K

1	**2**	**3**	**4**	**5**
34 378.7	26 436.8	33 140.6	34 408.8	35 301.0
34 379.2	26 428.8	33 154.1	34 406.2	35 289.3
34 380.0	26 428.6	33 174.4	34 391.4	35 286.1
34 384.8	26 446.8	33 147.2	34 399.9	35 284.7
34 389.6	26 443.7	33 161.4	34 397.6	35 304.8
	26 420.9	33 160.6		35 301.7
		33 150.4		
$-\langle\Delta_c u^\circ\rangle$J g^{-1}				
34 382.5 ± 2.1	26 434.3 ± 4.1	33 155.5 ± 4.2	34 400.8 ± 3.1	35 294.6 ± 3.6

Table 3 Derived molar values (kJ mol^{-1}) at 298.15 K

	1	**2**	**3**	**4**	**5**
$-\Delta_c U^\circ_m$(cr)	6024.8 ± 1.1	5821.6 ± 2.7	5344.8 ± 2.2	6028.0 ± 1.5	8375.4 ± 2.2
$-\Delta_c H^\circ_m$(cr)	6030.6 ± 1.1	5822.8 ± 2.7	5349.1 ± 2.2	6033.6 ± 1.5	8382.2 ± 2.2
$\Delta_f H^\circ_m$(cr)	−155.9 ± 1.8	−220.8 ± 3.1	−158.1 ± 2.6	−152.9 ± 2.1	−57.7 ± 3.0
$\Delta^g_{cr} H^\circ_m$(cr)	89.9 ± 3.8	121.9 ± 3.9	109.4 ± 2.4	99.2 ± 4.2	126.8 ± 3.0
$\Delta_f H^\circ_m$(g)	−66.0 ± 4.2	−98.9 ± 5.0	−48.7 ± 3.5	−53.7 ± 4.7	69.1 ± 4.2

Table 4 Selected interatomic distances (Å) and torsion angles (°)

	3	**4**	**2**
C(7)–O(1)	1.255(5)	1.252(4)	1.244(3)
C(8)–C(7)	1.406(6)	1.402(5)	1.429(4)
C(9)–C(8)	1.384(6)	1.385(5)	1.351(4)
N(1)–C(9)	1.324(6)	1.334(4)	1.362(3)
N(1)–H(N1)	0.97(5)	1.01(3)	0.78(2)
O(1)–H(N1)	1.96(5)	1.81(4)	1.97(3)
O(1)–C(7)–C(8)–C(9)	−5.9(8)	1.2(7)	2.1(5)
C(7)–C(8)–C(9)–N(1)	4.9(8)	−1.9(6)	−1.1(4)
C(2)–C(1)–C(7)–C(8)	−149.2(4)	—	—
C(6)–C(1)–C(7)–C(8)	—	160.4(4)	—
C(2)–C(1)–N(1)–C(9)	—	—	17.3(5)

selected interatomic distances and angles are given in Table 4. In each compound the atoms C(1), C(7), C(8), C(9), N(1) and H(N1) are coplanar.

Although hydrogen atom location by X-ray diffraction is not easy, the hydrogen atoms in all three compounds were sufficiently well located to show that tautomer **II** is present, not **I** or **III**, as can be seen from the N–H and O••• H distances in Table 4. The same conclusion is reached independently by examining the bond lengths C(7)–O(1), C(7)–C(8), C(8)–C(9) and C(9)–N(1) and comparing them with appropriate standard values.[21] In two compounds, **3** and **4** the bonds C(7)–C(8), C(9)–N(1) are shorter by about 0.03 Å than in the third compound **2**, while the bond C(9)–C(8) is a little longer in the first two compounds than in the third. This suggests that the electron distribution in the first two compounds is more delocalized than is shown by the single and double bonds in tautomer **II**; a better description would include a contribution from **IV**. Since positive charge on the nitrogen atom would be less favourable when there is a nitro-group substituent as in **2**, the contribution of **IV** would be less in this compound than in **3** or **4**,

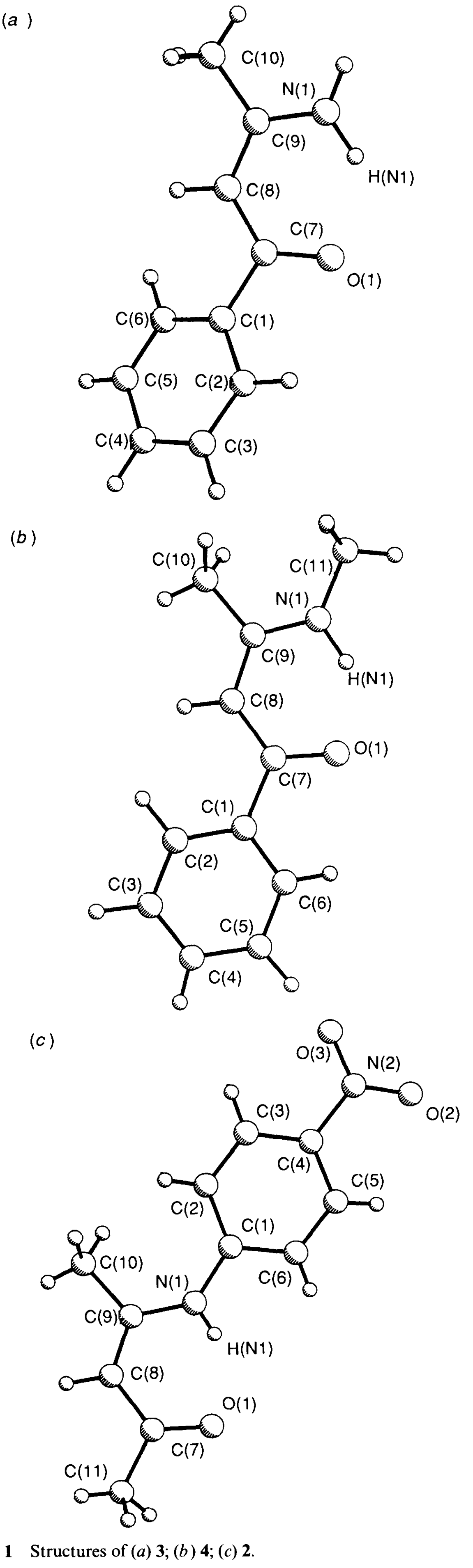
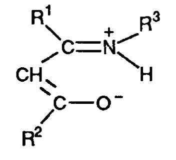


Fig. 1 Structures of (*a*) **3**; (*b*) **4**; (*c*) **2**.



IV

thus accounting well for the observed differences in bond lengths.

Application of bond-energy schemes to these compounds is problematical because of the lack of information on model compounds for comparison. It is possible however, to consider the enthalpy of the formation reaction in the gaseous state of the β-ketoimine from the β-diketone in the enol form and the corresponding amine, *i.e.* $\Delta_r H^\circ_m(g)$ for Scheme 1, requiring the

$$RCOCH{=}C(CH_3)OH + NH_2R^1 \longrightarrow RCOCH{=}C(CH_3)NHR^1 + H_2O$$

Scheme 1

following standard enthalpies of formation in kJ mol^{-1}: $H_2O(g)$, − 241.82 ± 0.04;[20] $CH_3COCH{=}C(CH_3)OH(g)$, −384.4 ± 1.3;[22] $C_6H_5COCH{=}C(CH_3)OH(g)$, −244.1 ± 2.9;[23] $NH_3(g)$, −45.94 ± 0.35;[20] $CH_3NH_2(g)$, −23.0 ± 0.5;[24] $C_6H_5NH_2(g)$, 87.1 ± 1.0;[25] 4-$NO_2C_6H_4NH_2(g)$, 58.8 ± 1.5.[26] The enthalpies of the formation reactions in kJ mol^{-1} are: **1** − 10.5 ± 4.5; **2**, − 15.1 ± 5.4; **3**, − 0.5 ± 4.6; **4**, −28.4 ± 5.5; **5**, −15.7 ± 5.2. The enthalpies of these formation reactions are small and for **1**, **2** and **5** are equal to within the limits of experimental uncertainty; they also show an increase in delocalization energy in the derivatives **3**, **4** and **5**, compared with the derivatives **1** and **2**, as is present between benzoylacetone and acetylacetone. Application of the Laidler bond-energy scheme with parameters given,[24] which include the delocalization energy of the phenyl group, lead to values for the delocalization energy of the ring atoms plus the intramolecular hydrogen bond energy for the enol form of acetylacetone, 115.8 kJ mol^{-1} and for benzoylacetone, 148.6 kJ mol^{-1}. This increase in delocalization energy of the derivatives **3**, **4** and **5** compared with the derivatives **1** and **2** is in accord with the crystal structure results which show greater delocalization in the former derivatives.

The order of the enthalpies of formation reactions of β-diketones with amines RNH_2 show a dependence on the group R and this order is in accord with that observed for corresponding reactions involving ethanoic acid, for substitution into a delocalized system, $CH_3CO_2H(g) + NH_2R(g) \rightleftharpoons CH_2CONHR(g) + H_2O(g)$. Calculation of $\Delta_r H^\circ_m(g)$ requires the following enthalpies of formation in kJ mol^{-1}: $CH_3CO_2H(g)$, −432.0 ± 0.5;[24] $CH_3CONH_2(g)$, −238.3 ± 0.8;[27] $CH_3CONHBu(g)$, −304.7 ± 2.1;[24] $CH_3CONHC_6H_5(g)$, −128.9 ± 1.7;[24] $BuNH_2g$, −95.0 ± 1.7;[24] giving $\Delta_r H^\circ_m(g)$ in kJ mol^{-1} for R = H, −2.2 ± 1.0; R = Bu, −19.5 ± 2.7; and for R = C_6H_5, −25.8 ± 2.0. Hence the enthalpies of formation of the β-ketoimines reported in this paper fall into an expected pattern when the enthalpies of their reactions are compared with those of analogous systems and are in accord with expectations from the crystal structure determinations.

Acknowledgements

Thanks are due to *Instituto Nacional de Investigação Científica* (*Lisboa*) for financial support to *Centro de Investigação em Química, Universidade do Porto* (Q.P.1., L.5 and L.6), to *Junta Nacional de Investigação Científica e Tecnológica* (*Lisboa*) for support to A. M. Damas and to SERC for financial support to the Chemistry Department, Liverpool University.

References

1 M. A. V. Ribeiro da Silva, *Thermochemistry and its Applications to Chemical and Biological Systems*, ed. M. A. V. Ribeiro da Silva, NATO ASI Series, Reidel, Dordtrecht, 1984, p. 317; M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, *Pure Appl. Chem.*, 1988, **60**, 1235.
2 K. Ueno and A. E. Martell, *J. Phys. Chem.*, 1955, **59**, 998; 1957, **61**, 257.
3 N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *J. Am. Chem. Soc.*, 1949, **71**, 3337.
4 D. F. Martin, G. A. Janusonis and B. B. Martin, *J. Am. Chem. Soc.*, 1961, **83**, 73.
5 H. F. Holtzclaw Jr., J. P. Collman and R. M. Alire, *J. Am. Chem. Soc.*, 1958, **80**, 1100.
6 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, M. C. S. S. Rangel, G. Pilcher, M. J. Akello, A. S. Carson and E. H. Jamea, *Thermochim. Acta*, 1990, **160**, 267.
7 E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1927, 1832.
8 J. Bickerton, G. Pilcher and G. Al-Takhin, *J. Chem. Thermodyn.* 1984, **16**, 373.
9 M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva and G. Pilcher, *Rev. Port. Quim.*, 1984, **26**, 163.
10 M. D. M. C. Ribeiro da Silva, M. A. V. Ribeiro da Silva and G. Pilcher, *J. Chem. Thermodyn.*, 1984, **16**, 1149.
11 W. N. Hubbard, D. W. Scott and G. Waddington, *Experimental Thermochemistry*, ed. F. D. Rossini, Interscience, New York, 1956, vol. 1, ch. 5.
12 The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, 1982, 11, Supplement no. 2.
13 Atomic Weights of the Elements, *Pure Appl. Chem.*, 1986, **58**, 1677.
14 F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, *J. Organomet. Chem.*, 1975, **97**, 221.
15 D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
16 C. G. de Kruif, T. Kuipers, J. C. van Miltenburg, R. C. F. Schaake and G. Stevens, *J. Chem. Thermodyn.*, 1981, **13**, 1081.
17 J. C. Calbrese, *Phase Patterson Heavy Atom Solution Extractor*, University of Wisconsin-Madison, Ph.D. Thesis, 1972.
18 P. T. Beurskens, DIRDF Direct Methods for Difference Structures: Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.
19 TEXSAN-TEXRAY, Structure Analysis Package, Molecular Structure Corporation, 1985.
20 CODATA, *J. Chem. Thermodyn.*, 1978, **10**, 903.
21 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
22 J. M. Hacking and G. Pilcher, *J. Chem. Thermodyn.*, 1979, **11**, 1015.
23 M. A. V. Ribeiro da Silva and M. J. S. Monte, *J. Chem. Thermodyn.*, 1992, **24**, 1219.
24 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970.
25 W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, *J. Chem. Eng. Data*, 1962, **7**, 229.
26 N. D. Lebedeva, N. M. Gutner and V. L. Ryadnenko, *Russ. J. Phys. Chem.*, 1971, **45**, 561.
27 D. S. Barnes and G. Pilcher, *J. Chem. Thermodyn.*, 1975, **7**, 377.

Paper 3/03028H
Received 27*th May* 1993
Accepted 22*nd June* 1993