Synthesis, characterization and thermochemical properties of *N*-acyl-*N*′,*N*′-diethylthioureas

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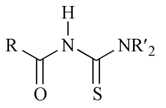
Three *N*-acyl-*N*′,*N*′-diethylthioureas, $RCONHCSNEt_2$, R = ^{i}Pr, ^{i}Bu, ^{t}Bu, have been prepared and characterised. The standard (p^o = 0.1 MPa) molar enthalpies of combustion in oxygen of the three crystalline compounds, at T = 298.15 K, have been measured by rotating bomb-combustion calorimetry, and the standard molar enthalpies of sublimation of the compounds by microcalorimetry. These values were used to derive the standard molar enthalpies of formation of the compounds in their crystalline and gaseous phases, respectively. The derived standard molar enthalpies of formation in the gaseous state are discussed comparatively. Acid constants and some complex stabilities have been measured pH-potentiometrically in dioxane–water mixture. The crystal structure of *N*,*N*-diethyl-*N*′-isovaleroyl-thiourea is presented and shows a delocalization of the π electrons of the C=S group over the carbon–amine nitrogen bond, $CS–NEt_2$, stabilising the molecule, in accordance with the thermochemical results.

Introduction

Acylchalcogenoureas are known for their use as metal complexing agents and they have been used for the separation of metals by selective sorption in chromatographic columns.[1–3] Their physico-chemical characteristics are of great interest since the knowledge of them allows one to choose the best working conditions in different fields. The ligand properties of these compounds depend greatly on the number and nature of the substituents at the terminal nitrogen atoms as well as on the acyl groups as, for example, acid constants of the molecules in solution and stability constants of the related metal complexes.[1,4–7]

The literature reports some solution calorimetric studies concerned with the acid strengths of ligands and the stability constants of the corresponding metal complexes[8,9] for some of this class of compounds, although there is only one paper[10] reporting values for the thermochemical properties of two *N*,*N*-dialkyl-*N*′-benzoylureas, $PhCONHCONR_2$ (R = Et, ^{i}Bu), both in condensed and gaseous phases. In this paper it is shown that the difference of the standard molar enthalpies of formation of the two compounds, which differ only by the alkyl substituents on the nitrogen atom, is the same as can be estimated applying the group energy contributions.

As part of a broad thermochemical study on acylchalcogenourea derivatives involving unsaturated bidentate 1-acyl-3,3-dialkylthiourea ligands, this paper reports synthesis, characterization and thermochemical work on the following three compounds: *N*,*N*-diethyl-*N*′-isobutanoylthiourea, ^{i}Pr-$CONHCSNEt_2$, HIPET, *N*,*N*-diethyl-*N*′-isovaleroylthiourea, $^{i}BuCONHCSNEt_2$, HIBET, and *N*,*N*-diethyl-*N*′-pivaloylthiourea, $^{t}BuCONHCSNEt_2$, HPVET, whose formulae are represented in Fig. 1.



with R′ = Et
R = ^{i}Pr (HIPET)
R = ^{i}Bu (HIBET)
R = ^{t}Bu (HPVET)

Fig. 1 Molecular formulae of acylated thioureas.

Knowledge of the standard molar enthalpies of formation of these acylated thioureas, both in the condensed and in the gaseous phases, is necessary not only for the thermochemical study of their metal complexes, but also to fill a gap in the available thermochemical data for this class of compounds, thus providing some reliable data for the estimation of thermochemical data for other compounds with similar structure. This is of particular importance in the study of the metal–ligand binding in these systems, which is very important in metal extraction processes.

The values of the standard (p^o = 0.1 MPa) molar enthalpies of formation, in the crystalline state, of these three compounds were derived from the respective enthalpies of combustion in oxygen, at T = 298.15 K, measured by rotating bomb calorimetry. The enthalpies of sublimation, at T = 298.15 K, were measured by Calvet microcalorimetry.

Experimental

Materials

The syntheses of the three $RCONHCSNR'_2$ compounds, which have not been described before, were performed according

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Table 1 Elemental analytical data and values for melting points

Compound	Found (%)				Calculated (%)				Mp/°C
	C	H	N	S	C	H	N	S	
HIPET	53.70	9.24	13.87	16.15	53.43	8.97	13.85	15.85	65–66
HIBET	55.74	9.42	13.01	14.70	55.52	9.32	12.95	14.82	86–88
HPVET	55.42	9.22	12.55	15.00	55.52	9.32	12.95	14.82	88–90

Table 2 ^{1}H and ^{13}C NMR spectra of ^{i}PrCONHCSNEt$_2$, HIPET, ^{i}BuCONHCSNEt$_2$, HIBET, and ^{t}BuCONHCSNEt$_2$, HPVET (Varian Gemini 2000, CDCl$_3$, internal TMS, T = 293 K)

HIPET	^{1}H NMR (200 MHz): δ 1.11 (d, J = 6.8 Hz, 6H), 1.23 (m, 6H), 2.50–2.60 (m, 1H), 3.43 (m, 2H), 3.91 (m, 2H), 8.70 (s, 1H); ^{13}C NMR (50 MHz): δ 11.9, 13.5, 19.3, 36.0, 48.1, 174.4, 180.1
HIBET	^{1}H NMR (200 MHz): δ 0.94 (d, J = 6.6 Hz, 6H), 1.25 (m, 6H), 2.14 (m, 1H), 2.18 (m, 2H), 3.50 (m, 2H), 3.91 (m, 2H), 8.61 (s, 1H); ^{13}C NMR (50 MHz): δ 12.1, 13.5, 22.8, 26.5, 46.3, 48.1, 170.1, 179.7
HPVET	^{1}H NMR (200 MHz): δ 1.23 (s, 9H), 1.28 (m, 6H), 3.47 (m, 2H), 3.92 (m, 2H), 7.26 (s, 1H); ^{13}C NMR (50 MHz): δ 12.0, 13.6, 27.6, 40.2, 48.3, 175.6, 180.4

to the general procedure described by Douglass *et al.*[11] for other acylthioureas. *N*,*N*-Diethyl-*N′*-isobutanoylthiourea, ^{i}PrCONHCSNEt$_2$, *N*,*N*-diethyl-*N′*-isovaleroylthiourea, ^{i}BuCONHCSNEt$_2$ and *N*,*N*-diethyl-*N′*-pivaloylthiourea, ^{t}BuCONHCSNEt$_2$ were prepared by adding a solution of anhydrous acetone containing potassium thiocyanate to the appropriate acyl chloride, RCOCl (2-methylpropanoyl chloride, isovaleroyl chloride or pivaloyl chloride, respectively). After stirring and warming the mixtures, a cold solution of dialkylamine, NHR′$_2$ (diethylamine) in acetone was added. The final mixtures were poured in a bath at 0 °C and the white crystals of the acylated thioureas were formed, then filtered and purified by recrystallization from ethanol–water. The compounds are stable at room temperature and they have been characterised by their melting points (Table 1), elemental analysis, IR spectroscopy and potentiometric pK_a measurements. The microanalytical results (obtained in Microanalytical Services of the University of Manchester) are given in Table 1. The ^{1}H NMR and ^{13}C NMR spectra confirm the expected structures of the compounds, showing also a split signal of the –CH$_2$– groups in the –CS–(NEt$_2$)– moiety based on the hindered rotation around the (CS)–N bond (see Table 2).

Crystal structure determination by X-ray analysis has been performed for *N*,*N*-diethyl-*N′*-isovaleroylthiourea, for which the crystals were grown from a solution of ethanol–water (1 : 1).

Combustion calorimetry

The combustion experiments for the three compounds were performed using a rotating bomb calorimeter originally from the National Physical Laboratory, Teddington, UK.[12] The apparatus, after having been installed in the University of Manchester, UK,[13] was transferred to Porto University, where some changes in the auxiliary equipment were made as previously described.[14] The rotating bomb calorimeter was used with a platinum-lined bomb of internal volume 0.337 dm^3. Water was added to the calorimeter from a weighted perspex vessel and for each experiment a correction to the energy equivalent was made for the deviation in the mass of water from 4059.0 g. The ignition temperature for each experiment was chosen so that the final temperature was close to T = 298.15 K. Rotation of the bomb was started when the temperature rise in the main period reached about 60% of its final value and was then continued throughout the rest of the experiment; so, according to the procedure of Good *et al.*,[15] the frictional work of bomb rotation was automatically included in the corrections for the heat exchange with the surrounding thermostat and the work of stirring.

Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190r) was used for the calibration of the bomb. The specific energy of combustion of this sample of benzoic acid is −(26432.3 ± 3.8) J g^{-1}, under certificate conditions. The calibration results were corrected to give the energy equivalent ε(calor) corresponding to the average mass of 4059.0 g water added to the calorimeter. From eight calibration experiments, ε(calor) = (20690.2 ± 6.6) J K^{-1} for the study of the compounds ^{i}PrCONHCSNEt$_2$ and ^{i}BuCONHCSNEt$_2$, or ε(calor) = (20675.2 ± 3.0) J K^{-1} for the study of ^{t}BuCONHCSNEt$_2$, the uncertainty quoted being the standard deviation of the mean. 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 $\mathrm{CH_{1.686}O_{0.843}}$, the massic energy of combustion is $\Delta_c u^o = -16250$ J g^{-1},[16] a value which has been confirmed in our laboratory. The corrections for nitric acid formation were based on −59.7 kJ mol^{-1},[17] for the molar energy of formation of 0.1 mol dm^{-3} HNO$_3$ (aq) from N$_2$, O$_2$ and H$_2$O (l).

The procedure described by Waddington *et al.*[18] for combustion calorimetry of organosulfur compounds was followed. The RCONHCSNR′$_2$ compounds were burned in pellet form in oxygen at p = 3.04 MPa with 10 cm^3 of water placed in the bomb. After each combustion experiment the amount of nitric acid was determined using Devarda's alloy; the amount of nitrous acid was found to be thermally insignificant. At T = 298.15 K, $(\partial u/\partial p)_T$ for these solids was assumed to be −0.2 J g^{-1} MPa^{-1}, a typical value for organic solids; the massic energy of combustion $-\Delta_c u^o$ was calculated by the procedure given by Hubbard *et al.*[19]

Enthalpies of sublimation

The enthalpies of sublimation were measured in Porto, using the vacuum sublimation drop microcalorimetric method:[20] samples, about 5 mg of each crystalline compound, contained in a thin glass capillary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel, in a high temperature Calvet microcalorimeter held at T = 363 K, in the case of the compounds HIPET and HIBET, and T = 366 K, in the case of the compound HPVET. The observed enthalpies of sublimation were corrected to T = 298.15 K, using the value of $\Delta_{298.15\,\mathrm{K}}^{T} H_m^o$ estimated by the Benson's Group Method,[21] using values from Stull *et al.*[22] The microcalorimeter was calibrated *in situ* for these measurements using the reported enthalpy of sublimation of naphthalene.[22] The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 1995.[23]

Potentiometric measurements

All measurements (alkalimetric titrations) were carried out under an argon atmosphere in 1,4-dioxane–water mixture (75% v/v), T = 298 K, ionic strength = 0.1 mol dm^{-3} [(CH$_3$)$_4$N]NO$_3$, (p$K_{\mathrm{H_2O}}$ = 16.74),[24] using automated titration equipment (PHM

Table 3 Typical combustion experimental results, at T = 298.15 K

	HIPET	HIBET	HPVET
m(cpd)/g	0.79291	0.90449	0.53903
m(fuse)/g	0.00493	0.00353	0.00461
ε_i/J K^{-1}	54.16	54.35	33.07
ε_f/J K^{-1}	54.33	54.79	32.89
$\Delta m(H_2O)$/g	−0.3	2.4	−11.7
(T_i/K) −273.15	23.7293	23.5772	24.1886
(T_f/K) −273.15	24.9729	25.0204	25.0659
ΔT_{ad}/K	1.20649	1.41031	0.84563
$-\Delta U$(IBP)/J	25025.2	29269.2	17469.0
$-\Delta U(HNO_3)$/J	62.09	73.73	48.48
ΔU(ign)/J	1.18	1.18	1.18
ΔU_Σ/J	22.28	25.32	10.10
$-m\Delta_c u^o$(fuse)/J	80.06	57.33	74.87
$-\Delta_c u^o$(cpd)/J g−1	31353.8	32187.0	32160.6

Table 4 Individual values of the massic energy of combustion, $-\Delta_c u^o$, at T = 298.15 K (p^o = 0.1 MPa). The mean values are represented by $\langle\Delta_c u^o\rangle$

HIPET	HIBET	HPVET
	$-\Delta_c u^o$/J g^{-1}	
31 356.7	32 185.8	32 160.6
31 353.8	32 181.2	32 164.6
31 354.4	32 193.2	32 147.1
31 344.7	32 208.8	32 153.5
31 371.7	32 194.4	32 147.4
31 346.2	32 187.0	32 144.8
		32 146.4
	$-\langle\Delta_c u^o\rangle$/J g$^{-1\,a}$	
31 354.6 ± 3.9	32 191.7 ± 4.0	32 152.1 ± 2.9

[a] Mean value and standard deviation of the mean.

84, ABU 80, Radiometer Copenhagen) driven online by an IBM compatible. As a cell a combination of G202B–K701 electrodes (Radiometer Copenhagen) was used. The cell was calibrated in terms of −lg [H$^+$] in dioxane–water mixture by titration of HNO_3 with KOH. Carbonate-free KOH solution was prepared by reaction of KCl with carbonate-free Ag_2O and was checked by pH titration using recrystallised amidosulfonic acid as a standard substance. The MINIQUAD 75A/B program[25] processed the potentiometric data. The calculated results were evaluated by means of the given statistical criteria sigma, σ^2, and R-factor.

Crystal structure determination of *N*,*N*-diethyl-*N*′-isovaleroyl-thiourea

A crystal with approximate dimensions 0.8 × 0.6 × 0.3 mm^3 was used for the X-ray diffraction studies. Crystal data: $C_{10}H_{20}N_2OS$, M = 216.34, monoclinic, a = 12.402 (8), b = 9.568 (4), c = 13.150 (6) Å and β = 124.59 (6)°; U = 1284.6 (11) Å^3, T = 293 K, space group $P2_1/c$, Z = 4, 12355 reflections measured, 2924 unique and 2419 were observed ($I > 2\sigma I$) and used in all calculations. The final $wR(F^2)$ was 0.14 (all data). The calculated density is D_x = 1.12 g cm^{-3}. CCDC reference number 164615. See http://www.rsc.org/suppdata/p2/b1/b104709b/ for crystallographic files in .cif or other electronic format.

The structure was solved using SHELXS97[26] and refined with SHELXL97.[27]

Results and discussion

Combustion calorimetry

Detailed results for a typical combustion experiment on each compound are given in Table 3; $\Delta m(H_2O)$ is the deviation of the mass of water added to the calorimeter from the mass assigned for ε(calor) (4059.0 g); ΔU_Σ is the correction to the standard state; the remaining terms are as previously described.[19] The internal energy for the isothermal bomb process, ΔU(IBP) was calculated according to eqn. (1),where ΔT_{ad} is the calorimeter

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon(\mathrm{calor}) + c_p(H_2O, \mathrm{l})\,\Delta m(H_2O)\}\,\Delta T_{ad} + \varepsilon_i(T_i - 298.15) + \varepsilon_f(298.15 - T_i - \Delta T_{ad}) + \Delta U(\mathrm{ign}) \quad (1)$$

temperature change corrected for heat exchange and the work of stirring, and the remaining terms are as previously described.[19] The individual values of $-\Delta_c u^o$ together with the mean and its standard deviation are given in Table 4. Table 5 lists the derived standard molar energies and enthalpies of combustion, $\Delta_c U^o_m$ (cr) and $\Delta_c H^o_m$ (cr) relate to the reaction (2) as

$$C_aH_bN_2SO\ (\mathrm{cr}) + (a + b/4 + 1)\ O_2\ (\mathrm{g}) + (116 - b/2)\ H_2O\ (\mathrm{l}) = a\,CO_2\ (\mathrm{g}) + N_2\ (\mathrm{g}) + H_2SO_4{\cdot}115\ H_2O\ (\mathrm{l}) \quad (2)$$

well as the standard molar enthalpies of formation, $\Delta_f H^o_m$ (cr), for the three compounds, in the crystalline state at T = 298.15 K. In accordance with the normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and formation are twice the overall standard deviation of the mean and include the uncertainties in calibration[28] and in the auxiliary quantities used. To derive $\Delta_f H^o_m$ (cr) from $\Delta_c H^o_m$ (cr) the standard molar enthalpies of formation of H_2O (l), of CO_2 (g) and H_2SO_4 *in* 115 H_2O (l), at T = 298.15 K, respectively, −(285.830 ± 0.042) kJ mol^{-1},[29] −(393.51 ± 0.13) kJ mol^{-1},[29] and −(887.81 ± 0.01) kJ mol^{-1}[17] were used.

Sublimation

Measurements of the enthalpies of sublimation, $\Delta^g_{cr}H^o_m$, are given in Table 6 with uncertainties of twice the standard deviation of the mean. The derived enthalpies of formation, in both crystalline and gaseous phases, at T = 298.15 K, for the compounds studied are also summarised in Table 6.

pK_a and lg β_n measurements

The three compounds behave as weak acids in solution. Their acid constants (see Table 7) are within the expected range of this class of compounds (*e.g.*, 1,1-diethyl-3-benzoylthiourea, pK_a = 10.87),[1] but they are less acidic because of the lack of the aromatic substituent and its delocalizing effect on the anionic charge. The small trend in pK_a values 11.93–12.06–12.12 (sequence HIBET–HIPET–HPVET) reflects the increasing shielding influence of the acyl part of the molecules against solvation of the polar molecule anion by the polar water and the polar parts of the cosolvent dioxane which would in turn also stabilise the anionic charge and thereby heighten the acidity.

The same is true for the stability constants of nickel complexes (1,1-diethyl-3-benzoylthiourea, lg β_2 = 15.32).[1] The stability constants of the copper complexes were found to be too high to be measured pH-potentiometrically (lg β_2 > 22) which is typical of the whole class of acyl-thioureas. Zinc complexes of the ligands investigated undergo hydrolysis during the titration experiments, showing the hydroxide ions to be stronger ligands than the organic anions. On the other hand, benzoyl substituted thioureas do form zinc complexes with stabilities similar to those of nickel. The stability constants (lg β_2) of the cadmium and lead complexes of HPVET that we measured as a probe are higher than those of 1,1-diethyl-3-benzoylthiourea by about half a logarithmic unit.

Crystallography

The three-dimensional structure of compound HIBET was determined and is presented in Fig. 2. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms converged to $R[F^2 > 2\sigma(F^2)] = 0.06$ and $wR = 0.14$. All hydrogen

Table 5 Derived standard molar energies of combustion, standard molar enthalpies of combustion and standard molar enthalpies of formation for ^{i}PrCONHCSNEt$_2$, HIPET, ^{i}BuCONHCSNEt$_2$, HIBET, and ^{t}BuCONHCSNEt$_2$, HPVET, at T = 298.15 K

	$-\Delta_c U_m^o$ (cr)/kJ mol^{-1}	$-\Delta_c H_m^o$ (cr)/kJ mol^{-1}	$\Delta_f H_m^o$ (cr)/kJ mol^{-1}
HIPET	6343.7 ± 2.7	6354.8 ± 2.7	−361.2 ± 3.0
HIBET	6964.6 ± 3.0	6977.0 ± 3.0	−418.4 ± 3.3
HPVET	6956.0 ± 1.9	6968.4 ± 1.9	−427.0 ± 2.3

Table 6 Derived standard molar enthalpies of formation and sublimation of ^{i}PrCONHCSNEt$_2$, HIPET, ^{i}BuCONHCSNEt$_2$, HIBET, and ^{t}BuCONHCSNEt$_2$, HPVET, at T = 298.15 K

	$\Delta_f H_m^o$ (cr)/kJ mol^{-1}	$\Delta_{cr}^{g} H_m^o$/kJ mol^{-1}	$\Delta_f H_m^o$ (g)/kJ mol^{-1}
HIPET	−361.2 ± 3.0	120.8 ± 2.5	−240.4 ± 3.9
HIBET	−418.4 ± 3.3	121.5 ± 3.2	−296.9 ± 4.6
HPVET	−427.0 ± 2.3	114.9 ± 2.7	−312.1 ± 3.6

Table 7 pK_a and lg β_n values, at T = 298.15 K; standard deviations 0.04 (pK_a), 0.05 (lg β_n)

	pK_a	Ni^{II}	Cd^{II}	Pb^{II}
HIPET	12.06	— lg β_2 = 15.47	Not measured	Not measured
HIBET	11.93	— lg β_2 = 14.51	Not measured	Not measured
HPVET	12.12	— lg β_2 = 16.48	lg β_1 = 7.31 lg β_2 = 14.78	lg β_1 = 8.14 lg β_2 = 15.72

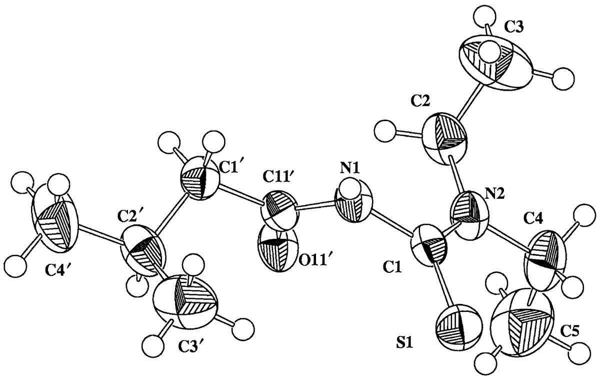

Fig. 2 The molecular structure of N,N-diethyl-N'-isovaleroylthiourea showing the atom-labelling scheme. H atoms are depicted as spheres of arbitrary radii. Displacement ellipsoids are shown at the 50% probability level.

atoms were found in the difference Fourier map and subsequently subjected to isotropic refinement. Tables containing the final fractional coordinates, temperature parameters, bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Centre, Cambridge, England (deposition number 164615).

The nitrogen (N1) to which the acyl group is attached is trigonal, exhibiting a C1–N1–C11′ angle of 121.5°. The N1–C bond lengths are different (1.433 and 1.359 Å), the acyl-substituted N1–C11′ distance being shorter. The N2–C bond lengths are also of unequal size (1.480, 1.476 and 1.323 Å), where the thiocarbonyl-substituted C1–N2 bond is shorter. These bonds are essentially the same as in compounds 1,1-diethyl-3-(4-methylbenzoyl)thiourea[30] and 1,1-diethyl-3-(2-chlorobenzoyl)thiourea.[31]

The O11′–C11′–N1–C1–S1 group is not planar, the dihedral angle between planes C1′–C11′–O11′–N1 and N1–C1–S1–N2 being 69.6 (1)°. The angle between the planes N1–C1–S1–N2 and C1–N2–C2–C4 is 4.5(1)°.

Selected bond lengths and angles are listed in Table 8.

The molecules in the crystal structure are held together by van der Waals forces and an intermolecular N–H···O hydrogen bond (N1H1···O11′^{i} is 2.06 Å)

Table 8 Selected bond lengths (Å) and angles (°) for N,N-diethyl-N'-isovaleroylthiourea

Bond	Length	Bond	Angle
S1–C1	1.672(2)	C1–N1–C11′	121.5(1)
C1–N1	1.433(2)	N1–C11′–O11′	121.6(2)
N1–C11′	1.359(2)	S1–C1–N1	118.3(1)
C11′–O11′	1.228(2)	N2–C1–S1	126.0(2)
C1–N2	1.323(2)	N2–C1–N1	115.7(2)
C11′–C1′	1.510(3)	C2–N2–C4	115.6(2)
N2–C2	1.480(2)	C2–N2–C1	124.5(2)
N2–C4	1.476(3)	C1–N2–C4	119.9(2)

A perspective view of the molecule showing the atomic numbering scheme was obtained using XPMA[32] and ORTEP[33] and is given in Fig. 2.

The three compounds RCONHCSNEt$_2$, with R = *i*Pr, *i*Bu, *t*Bu studied in this work differ only in the alkyl substituent of the acyl group, which enables us to compare the effect of the substituent R on the molecule, independently of the nature of the group R′ = Et.

The crystal structure of N,N-diethyl-N'-isovaleroylthiourea reveals a close agreement, in terms of bond lengths and angles, with the structures reported for other acylated thioureas, namely 1,1-diethyl-3-(4-methylbenzoyl)thiourea[30] and 1,1-diethyl-3-(2-chlorobenzoyl)thiourea.[31] As expected, C11′ of the acyl group is planar. However, while acylureas have planar C(O)NC(O)N groups, this acylthiourea has a twisted conformation, the angle defined by the planar C(O)N and NC(S)N being 69.58(0.09)°.

The increment in $\Delta_f H_m^o$ (g) is sensitive to the nature of the group R, although it cannot be predicted directly by a bond energy scheme introducing the energetic parameter from an identical substitution on an amine derivative. Considering the values available in the literature for $\Delta_f H_m^o$ (g) of 2-methylpropanamide, ^{i}PrCONH$_2$, and 2,2-dimethylpropanamide, ^{t}BuCONH$_2$, respectively −(282.6 ± 0.9) kJ mol^{-1}[34] and −(313.1 ± 1.4) kJ mol^{-1},[34] the derived increment for changing ^{i}Pr to ^{t}Bu is −(30.5 ± 1.7) kJ mol^{-1}. For the corresponding acylthiourea derivatives, ^{i}PrCONHCSNEt$_2$ and ^{t}BuCONHCSNEt$_2$, the increment is −(71.7 ± 5.3) kJ mol^{-1}, which suggests an additional stabilisation on the molecules under study. It is apparent that the energetic effect of the stabilisation between the π electrons of the thiocarbonyl bond is very significant, particularly due to the fact of the C=S group being adjacent to two nitrogen atoms. From the crystal structure of N,N-diethyl-N'-isovaleroylthiourea, we found that the bond lengths between the nitrogen atoms and the C=S group are different, the N2–CS being the shortest and with a value close to a double bond or to the typical value for the group CO–NH in a peptide. This result is consistent with a delocalization of the C=S bond over the S=C–N group.

The experimental values of $\Delta_f H_m^o$ (g) available for this class of 1-acyl-3,3-diethylthiourea are insufficient to be a basis for a bond-energy scheme to estimate the values of other $\Delta_f H_m^o$ of the other acyldialkylthioureas, particularly due to the lack of literature data on other similar compounds. This is also the situation for the thermochemistry of acyldialkylureas, for which only two compounds have been published.[10] In a previous work, we reported the enthalpies of formation, in the gaseous state, for the compounds PhCONHCON(^{i}Bu)$_2$ and PhCONHCSN(^{i}Bu)$_2$, respectively as $-(445.3 \pm 7.5)$ kJ mol^{-1}[10] and $-(164.8 \pm 4.9)$ kJ mol^{-1},[35] which enabled us to derive the increment for changing C=O to C=S, for the pair PhCONHCON(^{i}Bu)$_2$–PhCONHCSN(^{i}Bu)$_2$, as (280.5 ± 8.9) kJ mol^{-1}. This increment is consistent, although larger, with those of identical changes in the pairs acetamide[36]–thioacetamide[37] (251.0 ± 1.4) kJ mol^{-1}, benzamide[38]–thiobenzamide[13] (248.7 ± 3.0) kJ mol^{-1} and urea[39]–thiourea[40] (258.4 ± 2.0) kJ mol^{-1}. We understand the additional 280–258 = *ca.* 22 kJ mol^{-1} stabilisation of the acylurea over the acylthiourea arising from the destabilisation of the acylthiourea. While the acylurea has a totally planar –C(O)–NH–C(O)–N< skeleton, our crystallographic study shows that the corresponding acylthiourea –C(O)–NH–C(S)–N< skeleton is significantly twisted. This twisting results in poorer π overlap and so in less resonance stabilisation for the acylthiourea. At the current time there are no thermochemical data for planar acylthioureas and corresponding acylureas and so this interpretation remains somewhat speculative.

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