Aspects of the Aromaticity of Anthranil

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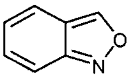
The standard ($p° = 0.1$ MPa) molar enthalpy of formation of liquid anthranil was measured at $T = 298.15$ K by static bomb calorimetry and the standard molar enthalpy of vaporization at $T = 298.15$ K was obtained using Calvet microcalorimetry. These values were used to derive the standard molar enthalpy of formation of anthranil in the gaseous phase. Thermochemical and quantum chemical comparisons were made to interrelate anthranil and its isomers, 1,2-benzisoxazole, benzoxazole and 2-cyanophenol, and the monocyclic heterocycles, isoxazole and oxazole. Comparisons with benzofurazan and isobenzofuran were also made. Additionally nucleus-independent chemical shifts were used as an aromaticity index.

Introduction

Anthranil (**I**) is a compound that has been known for a long time with a name that misleadingly links this species with anthracene and aniline: it is neither a derivative of a polynuclear hydrocarbon nor of an aromatic amine. Rather it is a highly unsaturated bicyclic nitrogenous heterocycle with 10π electrons and a single, classical resonance structure. We ask "is it aromatic?", for this species is π-isoelectronic/isoconjugate with its isomers 1,2-benzisoxazole (**II**) and benzoxazole (**III**), as well as with quinoline (**IV**) and isoquinoline (**V**) for which the presence of aromaticity seems unambiguous. On the other hand, the carbon−carbon bond conjoining the two rings is an essential single bond in that, like the corresponding bond in azulene (**VI**) and the Ph−Ph bond in biphenyl (**VII**), it is always a single bond in any resonance structure lacking a long bond (cf. the "Dewar" structure) or a dipolar/zwitterionic description. The current study reports the enthalpy of formation of anthranil as found by contemporary calorimetric measurements, and by means of both experimentally measured values and quantum chemical calculations, contrasts anthranil with the aforementioned isomers as well as with other related species.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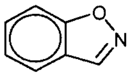
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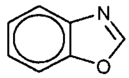
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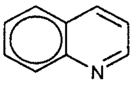
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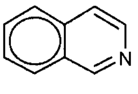
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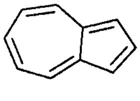
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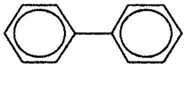
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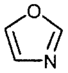
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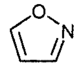
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In the Exp. Sect., we report the standard molar energy of combustion of anthranil (2,1-benzisoxazole, benz[*c*]isoxazole) determined using a static bomb calorimeter and the standard molar enthalpy of vaporization measured using a Calvet microcalorimeter. From these experimental results, the standard molar enthalpy of formation of anthranil in the gas phase, at $T = 298.15$ K, has been derived.

The equilibrium geometries of anthranil and its isomeric compounds, 1,2-benzisoxazole (benz[*d*]isoxazole), benzoxazole and 2-cyanophenol, and of the two isomers, the monocyclic oxazole (**VIII**) and isoxazole (**IX**), have been determined from density functional theory using the B3LYP functional and two basis sets: 6-31G* and 6-311G**. More accurate energies were also obtained from single-point calculations of the most stable B3LYP/6-311G** geometries, using the triple-zeta correlation consistent basis set, cc-pVTZ and the B3LYP functional.

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Table 1. Results of the combustion experiments of anthranil at $T = 298.15$ K[a]

m(CO_2, total) [g]	1.55267	1.63794	1.19044	1.68320	1.25882	1.75633
m(cpd) [g]	0.55323	0.58655	0.41296	0.60441	0.44991	0.63399
m(Melinex) [g]	0.05077	0.05058	0.05129	0.04976	0.04008	0.04958
m(fuse) [g]	0.00350	0.00320	0.00309	0.00380	0.00216	0.00198
ΔT_{ad} [K]	1.12209	1.18296	0.85662	1.21701	0.90973	1.27103
ε_f [$J \cdot K^{-1}$]	15.45	15.51	15.25	15.51	15.25	15.53
Δm(H_2O) (g)	−0.1	0.0	−0.2	0.0	0.0	0.0
$-\Delta U$(IBP) [J]	17974.73	18950.43	13721.36	19495.93	14572.91	20361.38
$-\Delta U$(HNO_3) [J]	40.36	41.07	29.79	44.83	35.40	49.07
$-\Delta U$(carbon) [J]	0.00	0.00	0.00	0.00	0.00	0.00
ΔU(ign) [J]	1.19	1.19	1.19	1.19	1.19	1.19
$-\Delta U_\Sigma$ [J]	12.95	13.70	9.75	14.09	10.32	14.71
$-\Delta U$(Melinex) [J]	1162.80	1158.46	1174.68	1139.50	917.90	1135.38
$-\Delta U$(fuse) [J]	56.84	51.97	50.18	61.71	35.08	32.16
$-\Delta_c u^\circ$(cpd) [$J \cdot g^{-1}$]	30189.58	30151.27	30165.05	30171.24	30170.95	30174.07
$<\Delta_c u^\circ> = -(30170.4 \pm 5.1)$ $J \cdot g^{-1}$ (0.017%)						

[a] m(CO_2, total) = total mass of CO_2 formed in the experiment; m(cpd) = mass of compound burnt in the experiment; m(Melinex) = mass of Melinex burnt in the experiment; m(fuse) = mass of fuse (cotton) used in the experiment; ΔT_{ad} = corrected temperature rise; ε_f = energy equivalent of contents in the final state; Δm(H_2O) = deviation of the mass of water added to the calorimeter from 3119.6 g; ΔU(IBP) = energy change for the isothermal combustion reaction under actual bomb conditions and includes ΔU(ign); ΔU(HNO_3) = energy correction for nitric acid formation; ΔU(carbon) = energy correction for carbon formation; ΔU(ign) = energy of combustion of the fuse; ΔU_Σ = energy correction to the standard state; ΔU(fuse) = energy of combustion of the fuse (cotton); ΔU(Melinex) = energy of combustion of the Melinex; $\Delta_c u^\circ$ = standard massic energy of combustion.

Results and Discussion

Experimental Results

Table 1 lists the results of the combustion experiments of anthranil, in which combustion occurs by Equation (1).

$$C_7H_5NO\ (l) + 31/4\ O_2\ (g) \rightarrow 7\ CO_2\ (g) + 5/2\ H_2O\ (l) + 1/2\ N_2\ (g) \quad (1)$$

The symbols in the table are as described previously.[1] Combustion experiments were performed in oxygen at $p = 3.04$ MPa with 1.00 cm^3 of water added to the bomb. As samples were ignited at $T = 298.15$ K, Equation (2) can be derived, where ΔU(IBP) is the energy associated with the isothermal bomb process, Δm(H_2O) is the deviation of the mass of water added to the calorimeter from 3119.6 g, c_p(H_2O, l) is the specific heat capacity of liquid water, ε_f is the energy of the bomb's contents after ignition, ΔT_{ad} is the adiabatic temperature rise and ΔU_{ign} is the energy of ignition.

$$\Delta U(\mathrm{IBP}) = -[\varepsilon_{cal} + \Delta m(H_2O) \cdot c_p(H_2O, l) + \varepsilon_f] \cdot \Delta T_{ad} + \Delta U_{ign} \quad (2)$$

For the cotton-thread fuse, the empirical formula $CH_{1.686}O_{0.843}$ and $\Delta_c u^\circ = -16250\ J \cdot g^{-1}$ were used.[2] The corrections for nitric acid formation ΔU(HNO_3) were based on a value of $-59.7\ kJ \cdot mol^{-1}$, for the molar energy of formation of 0.1 $mol \cdot dm^{-3}$ HNO_3(aq) from N_2, O_2, and H_2O(l).[3] Sealed Melinex bags were used in the combustion of the liquid compound using the technique described by Skinner and Snelson,[4] who determined the specific energy of combustion of dry Melinex to be $\Delta_c u^\circ = -(22902 \pm 5)\ J \cdot g^{-1}$. This value was confirmed in our laboratory.

The mean value of the standard massic energy of combustion is $<\Delta_c u^\circ> = -(30170.4 \pm 5.1)\ J \cdot g^{-1}$ at $T = 298.15$ K. The derived standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation of the compound in the liquid phase are $\Delta_c U^0_m(l) = -(3594.0 \pm 1.8)$, $\Delta_c H^0_m(l) = -(3594.6 \pm 1.8)$ and $\Delta_f H^0_m(l) = (125.5 \pm 2.0)\ kJ \cdot mol^{-1}$, respectively. In accordance with customary thermochemical practice,[5] the uncertainty assigned to the standard molar enthalpy of combustion is twice the overall standard deviation of the mean and includes the uncertainties in calibration and in the values of auxiliary quantities. To derive $\Delta_f H^0_m(l)$ from $\Delta_c H^0_m(l)$, the standard molar enthalpies of formation of CO_2(g) [$-(393.51 \pm 0.13)\ kJ \cdot mol^{-1}$] and H_2O(l) [$-(285.830 \pm 0.042)\ kJ \cdot mol^{-1}$] at $T = 298.15$ K were used.[6]

The observed enthalpy of vaporization, $\Delta^{g,T}_{l,298.15\,K} H^0_m$, at $T = 364$ K was corrected to $T = 298.15$ K using Equation (3), where $C^\circ_{p,m}$(g) is defined by Equation (4), which was derived from statistical thermodynamics using the vibrational frequencies obtained from the B3LYP/6-31G* calculations (see Computational Details in the Exp. Sect.).

$$\Delta^{T}_{298.15\,K} H^\circ_m(g) = \int_{298.15\,K}^{T} C^o_{p,m}(g)\,dT \quad (3)$$

$$C^\circ_{p,m}(g) = -0.000335T^2 + 0.606T - 45.696 \quad (4)$$

The resultant value of $\Delta^{364K}_{298.15\,K} H^0_m(g)$ is 7.8 $kJ \cdot mol^{-1}$. The standard molar enthalpy of vaporization at $T =$

298.15 K, $\Delta_f^g H_m^0$ (298.15 K) = (55.3 ± 0.7) kJ·mol^{-1}, was determined from six experiments (the uncertainty is twice the standard deviation of the mean), which enables the calculation of the standard molar enthalpy of formation of anthranil in the gaseous phase, $\Delta_f H_m^0$(g) = (180.8 ± 2.1) kJ·mol^{-1}.

The measurement of the enthalpies of combustion and vaporization of 1,2-benzisoxazole is precluded because of the photochemical instability of this isomer of anthranil, and hence the presumed lack of reproducibility and reliability of measurements such as ours.

Theoretical Results

The total energies, identified by the subscripts B3LYP/6-31G*, B3LYP/6-311G**, and B3LYP/cc-pVTZ, and the zero-point vibrational energies (ZP) and thermal energy corrections are reported in Table 2 for all the isomers. Perhaps not altogether surprisingly, the ZP energies and the thermal corrections are very nearly the same for the isomeric pair of compounds, oxazole and isoxazole, and for the isomeric triplet of anthranil, 1,2-benzisoxazole and benzoxazole.

The calculated energies at T = 0 K for Equations (5)−(11) are presented in Table 3. To compare the theoretical with the experimental results the reaction enthalpies were calculated from the individual molecular energies by adding the zero-point vibrational energies and the thermal corrections from T = 0 K to T = 298.15 K. The reaction enthalpies at T = 298.15 K are also presented in Table 3, together with the derived experimental reaction enthalpies obtained from the experimental standard enthalpies of formation, at T = 298.15 K, of the compounds involved in the reactions (the experimental standard enthalpies of formation of the auxiliary molecules were taken from ref.[7]).

For the isomerization reactions (5) and (6), we obtain an experimental value for $\Delta_r H$ of −(136.0 ± 2.2) kJ·mol^{-1} for the former and −(94.1 ± 0.7) kJ·mol^{-1} for the latter.

anthranil → benzoxazole (5)

isoxazole → oxazole (6)

These values are in good agreement with the results of our calculations and allow us to attribute the observed difference to a change in aromaticity of about (41.9 ± 2.3) kJ·mol^{-1}.

By regarding reaction (7) as the sum of reactions (5) and (6), an experimental value of $\Delta_r H$ of −(41.9 ± 2.3) kJ·mol^{-1} is obtained, which is the result of a balancing of isomerization energies and aromaticity change.

anthranil + oxazole → benzoxazole + isoxazole (7)

So it seems that the hypothetical reaction (8) should essentially be thermoneutral, because isomerization energies plausibly cancel (1,2-benzisoxazole → benzoxazole; oxazole → isoxazole) and also because there is no particular difference in aromaticity between the reagents and the products.

1,2-benzisoxazole + oxazole → benzoxazole + isoxazole (8)

Table 2. Calculated electronic energies [hartree], zero-point vibrational energies and thermal corrections to T = 298.15 K [kJ·mol^{-1}]

Compound	$E_{\mathrm{B3LYP/6\text{-}31G^*}}$	$E_{\mathrm{B3LYP/6\text{-}311G^{**}}}$	$E_{\mathrm{B3LYP/cc\text{-}pVTZ}}$ [a]	$E_{\mathrm{ZP/B3LYP/6\text{-}31G^*}}$	$E_{\mathrm{total/B3LYP/6\text{-}31G^*}}$ [b]
Anthranil	−399.665316	−399.766783	−399.811293	265.82	281.89
1,2-Benzisoxazole	−399.683056	−399.784384	−399.828909	266.18	282.14
Benzoxazole	−399.723244	−399.825882	−399.870035	267.86	283.59
2-Cyanophenol[c]	−399.711801	−399.824851	−399.868516	261.78	281.22
Oxazole	−246.069885	−246.138055	−246.165518	148.26	157.81
Isoxazole	−246.034711	−246.101524	−246.129316	146.69	156.33

[a] $E_{\mathrm{B3LYP/cc\text{-}pVTZ//B3LYP/6\text{-}311G^{**}}}$. [b] E_{total} (T = 298.15 K) = $E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{ZP}} + \Delta_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} E_{\mathrm{vib}}$. [c] The energies refer to the most stable *cis* rotamer.

Table 3. Calculated reaction energies at T = 0 K and enthalpies at T = 298.15 K

	$\Delta_r E_T$ = 0 K [kJ·mol^{-1}]			$\Delta_r H_T^0$ = 298.15 K [kJ·mol^{-1}]			
	6-31G*	6-311G**	cc-pVTZ	6-31G*	6-311G**	cc-pVTZ	Exp.[a]
Reaction (5)	−152.1	−155.2	−154.2	−150.4	−153.5	−152.5	−(136.0 ± 2.2)
Reaction (6)	−92.3	−95.9	−95.0	−90.9	−94.4	−93.6	−(94.1 ± 0.7)
Reaction (7)	−59.7	−59.3	−59.2	−59.5	−59.0	−59.0	−(41.9 ± 2.3)
Reaction (8)	−13.2	−13.0	−12.9	−13.2	−13.1	−13.0	−
Reaction (9)	−46.6	−46.2	−46.3	−46.3	−46.0	−46.0	−
Reaction (10)	−122.0	−152.5	−150.2	−122.7	−153.1	−150.9	−(148.0 ± 3.0)
Reaction (11)	−75.5	−106.2	−104.0	−76.4	−107.2	−104.9	−(112 ± 8.4)[8]

[a] Experimental enthalpies of formation for auxiliary compounds taken from ref.[7] The experimental value for reaction (11) refers to aqueous alcohol solution phase.

Theoretical calculations give a value of about -13 kJ·mol^{-1} for this reaction, in good agreement with these assumptions. Note that the theoretical value of Δ_rH for reaction (7) is about -59 kJ·mol^{-1} (Table 3), which is a deviation of -17 kJ·mol^{-1} from the experimental value.

From the thermoneutral reaction (8) and by using the enthalpies of formation[7a] of the gaseous species involved [oxazole: $-(15.5 \pm 0.5)$ kJ·mol^{-1}; isoxazole: (78.6 ± 0.5) kJ·mol^{-1}; benzoxazole: (44.8 ± 0.5) kJ·mol^{-1}] we estimate the enthalpy of formation of 1,2-benzisoxazole to be (138.9 ± 5) kJ·mol^{-1}.

Similarly, for Equation (9) we estimate a value of Δ_rH of about $-(41.9 \pm 2.3)$ kJ·mol^{-1} [the theoretical results for reaction (9) of ca. -46 kJ·mol^{-1} confirm this estimation] and consequently we obtain a value of (138.9 ± 3.1) kJ·mol^{-1} for the enthalpy of formation of 1,2-benzisoxazole.

$$\text{anthranil} \rightarrow \text{1,2-benzisoxazole} \qquad (9)$$

To confirm this estimate, we considered the ring-opening isomerization reaction (10) for which the experimental value for Δ_rH is $-(148.0 \pm 3.0)$ kJ·mol^{-1}, in good agreement with the theoretical calculation, allowing a value of about $-(106.1 \pm 3.8)$ kJ·mol^{-1} [$= -(148.0 \pm 3.0) + (41.9 \pm 2.3)$ kJ·mol^{-1}] to be estimated for the enthalpy of reaction (11), which involves the ring opening of 1,2-benzisoxazole.

$$\text{anthranil} \rightarrow \text{2-cyanophenol} \qquad (10)$$

$$\text{1,2-benzisoxazole} \rightarrow \text{2-cyanophenol} \qquad (11)$$

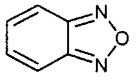
Reaction (11) was also studied in the liquid phase (aqueous alcohol) and the value of Δ_rH is $-(112 \pm 8)$ kJ·mol^{-1},[8] not that different from the one we have considered above. This is not too strange if the isomers have similar solvation energies.

From the value of $\Delta_rH(11)$ [$-(106.1 \pm 3.8)$ kJ·mol^{-1}] and the enthalpy of formation of 2-cyanophenol [(32.8 ± 2.1) kJ·mol^{-1}],[7b] we estimate a value of (138.9 ± 4.3) $\text{kJ·mol}^{-1}$for the enthalpy of formation of 1,2-benzisoxazole.

Another interesting comparison involves reaction (12).

$$\text{benzofurazan} + \text{isobenzofuran} \rightarrow 2\ \text{anthranil} \qquad (12)$$

Naively, by neglecting any differential aromaticity effects in the rings and the N−O−N anomeric interaction found only in benzofurazan (**X**), we are tempted to suggest that this reaction should be thermoneutral. There are three measurements for the enthalpy of formation of gas-phase benzofurazan: (302.3 ± 2.1),[9a] (300.7 ± 2.1)[9b] and 272.7[9c] kJ·mol^{-1}. Neglecting the third value because of "age" and a lack of consensus, we take a value of (301 ± 3) kJ·mol^{-1}. No measurements have been reported for isobenzofuran (**XI**). However, the enthalpy of formation of its 1,3-diphenyl derivative, in which both the carbon atoms adjacent to the oxygen atom have been phenylated, in the gas phase is reported to be (203 ± 10) kJ·mol^{-1}.[10] Assuming that the same phenylation enthalpy as found in the series benzene, biphenyl, the isomeric terphenyls and isomeric quaterphenyls [(97.3 ± 1.3) kJ·mol^{-1}][11] applies to the series isobenzofuran, 1-phenylbenzoisofuran and 1,3-diphenylbenzoisofuran, we conclude that isobenzofuran should have an enthalpy of formation of about (8 ± 11) kJ·mol^{-1}. This suggests that anthranil should have an enthalpy of formation of about (155 ± 12) kJ·mol^{-1}. This value is much lower than the value we reported above [(180.8 ± 2.1) kJ·mol^{-1}], but it is not altogether different given the instability and reactivity of benzofurazan and the disubstituted isobenzofuran.



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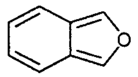
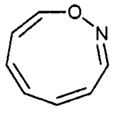
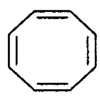


XI

One may regard both isomers anthranil and 1,2-benzisoxazole as derivatives of 1,2-oxazonine (i.e., 1-oxa-2-aza-2,4,6,8-cyclononatetraene, **XII**) with an additional transannular C−C bond that transforms this monocycle into a bicyclic species with five- and six-membered rings. In the absence of any other information (such as resonance, nay aromatic, stabilization associated with Kekulé resonance structures), one would assume that these two bicyclic species would have very similar enthalpies of formation. In fact, as enunciated above, our studies show that the difference is about 42 kJ·mol^{-1}. This difference is significant, but is far less than the nearly identical values of about 140 kJ·mol^{-1} by which naphthalene is more stable than its aromatic isomer azulene and benzene is more stable than the nonaromatic "6/8-cyclooctatetraene" (**XIII**).[11] This suggests that by thermochemical criteria, if we ascribe aromatic character to 1,2-benzisoxazole, then we should ascribe significant aromatic character to anthranil as well.



XII



XIII

We have calculated the NICS (nucleus-independent chemical shift) values for the molecules involved in our study of anthranil: Analysis of these values provides a magnetic criterion for aromaticity.[12] The values were calculated using RHF/6-31+G* wavefunctions of the most stable B3LYP/6-311G** geometries and are presented in Table 4. There are two values for each ring and each molecule: one at the geometrical centre of the ring (i.e. the point whose coordinates are the nonweighted mean of the homologous coordinates of the heavy atoms of the rings), denoted NICS(0), and 0.5 Å above the centre of the ring, denoted NICS(0.5). The NICS values calculated above the ring and on the ring are in very good agreement and both sets of values indicate that all the species have aromatic character since they have negative values. The benzenic rings of these systems, with the exception of anthranil, shows NICS values that are consistent with the value found for benzene itself with the same basis set and wavefunctions [NICS(0) = −9.7], but they are slightly more negative. Similar comparisons apply to the NICS calculated at the centre of the five-membered rings, which compare with the values found for pyrrole (−15.1) and furan (−12.3).[12] The NICS values for anthranil are remarkably different to those of the other compounds studied in this work; anthranil has a larger NICS value for the six-membered ring and a correspondingly lower value for the five-membered ring. This indicates a loss of aromaticity in the six-membered ring and an increase in the aromaticity of the five-membered ring, which seems to be in agreement with our calculations which suggest that anthranil is less benzenoid than its isomeric molecules. Benzene and 2-cyanophenol (as well as the monosubstituted phenol and benzonitrile) are not that different in terms of aromaticity. Even benzoxazole and 1,2-benzisoxazole are not that different in terms of their six-membered rings. What about anthranil? Interestingly, in that the sum of the NICS values [(0.0) or (0.5)] for the five- and six-membered rings in anthranil is very nearly the same as those for its isomers 1,2-benzisoxazole and benzoxazole, it would appear that the aromaticity of these three species are very nearly the same as well.

Table 4. Nucleus independent chemical shifts (ppm)

[a]	6-membered ring		5-membered ring	
	NICS(0)	NICS(0.5)	NICS(0)	NICS(0.5)
Anthranil	−4.9	−6.4	−14.5	−15.2
1,2-Benzisoxazole	−11.1	−12.5	−9.9	−10.7
Benzoxazole	−12.2	−13.3	−8.6	−9.4
2-Cyanophenol	−10.7	−11.7	–	–
Oxazole	–	–	−11.3	−11.5
Isoxazole	–	–	−12.1	−12.6
Phenol	−10.7	−11.9	–	–
Benzene	−9.7	−11.5	–	–
Benzonitrile	−10.3	−11.9	–	–
Naphthalene	−9.9	−11.6	–	–

[a] For the nonplanar 1,2-oxazonine: NICS(0) = −1.5; NICS(+0.5) = −2.4; NICS(−0.5) = −2.4.

Experimental Section

Materials: Anthranil (2,1-benzisoxazole, CAS number 271-58-9) is a commercial product from Aldrich Chemical Co., with a mass fraction of 99.9% (GLC), and was further purified by vacuum distillation until the combustion results were consistent and the carbon dioxide recovery ratios were satisfactory. The average ratio, together with the standard deviation of the mean, of the mass of carbon dioxide recovered to that calculated from the mass of the sample was (1.0000 ± 0.0002). The purity of the liquid was also assessed by GLC. The density was taken as $\rho = 1.183\ \mathrm{g \cdot cm^{-3}}$.[13]

Combustion Calorimetry: The combustion experiments were performed with a static bomb calorimeter. The apparatus and technique have been described previously.[14,15] Benzoic acid (Bureau of Analysed Samples, Thermochemical Standard, BCS-CRM-190) was used for calibration of the bomb. Its massic energy of combustion is $\Delta_c u = -(26435.1 \pm 3.5)\ \mathrm{J \cdot g^{-1}}$ under certificate conditions. The calibration results were corrected to give the energy equivalent ε_{cal} corresponding to the average mass of water added to the calorimeter, 3119.6 g. From the six calibration experiments that were performed, $\varepsilon_{cal} = (16005.0 \pm 2.0)\ \mathrm{J \cdot K^{-1}}$, where the uncertainty quoted is the standard deviation of the mean. Sealed Melinex bags were used in the combustion of the liquid compound using the technique described by Skinner and Snelson.[4]

Calvet Microcalorimetry: The standard molar enthalpy of vaporization was measured using the "vacuum sublimation" drop microcalorimetric method,[16] which, in the case of vaporization, was previously tested in the Porto laboratory.[17] Samples, about 7−10 mg of liquid, in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot reaction vessel in a high-temperature Calvet microcalorimeter held at a convenient temperature, $T = 364$ K, and then removed from the hot zone by vacuum vaporization. The microcalorimeter (Calvet High Temperature Microcalorimeter, SETARAM HT 1000) was calibrated in situ for these measurements using the reported standard molar enthalpy of vaporization of decane at $T = 298.15$ K [(51.42 ± 0.21) $\mathrm{kJ \cdot mol^{-1}}$].[18] Accuracy tests were performed with undecane whose reported standard molar enthalpy of vaporization at $T = 298.15$ K is (56.58 ± 0.57) $\mathrm{kJ \cdot mol^{-1}}$.[18]

Computational Details: The geometries of all molecules were fully optimised using the density functional theory (DFT) based on the Becke-3-parameter hybrid exchange[19] and Lee−Yang−Parr[20] correlation density functional (B3LYP) and two different basis sets: 6-31G*[21,22] and 6-311G**.[23,24] The harmonic vibrational frequencies were obtained from the optimum B3LYP/6-31G* geometries using the same basis set and were scaled by a factor of 0.9614[25] in order to correct for anharmonicity. More accurate energies were also obtained with the 6-311G** geometries using the triple-zeta correlation consistent basis set, cc-pVTZ.[26] All calculations were performed using the UK version of GAMESS.[27,28] The NICS values were calculated using RHF/6-31+G* wavefunctions derived from the B3LYP/6-311G** geometries. The methodology used was developed by von R. Schleyer and co-workers.[12] Two different values were calculated for each ring and each molecule: one at the geometrical centre of the ring (i.e. the point whose coordinates are the nonweighted mean of the homologous coordinates of the heavy atoms of the rings), denoted NICS(0), and 0.5 Å above the center of the ring, denoted NICS(0.5).

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