# Heat of Combustion of Some *N*-Heterocycle Compounds. Part 1

**Muayyad Faour and Talal S. Akasheh** *
*Chemistry Department, Yarmouk University, Irbid, Jordan*

The heats of combustion of triazole, indazole, 2,2′-bipyridine, and 2,2′-biquinoline are reported (1 328.9 ± 1.2, 3 778.6 ± 3.5, 5 285.5 ± 4.7, 9 049.4 ± 6.8 kJ $mol^{-1}$, respectively). This leads to evaluation of heats of formation and atomisation. Allen-type resonance energies are also calculated and compared with those of similar compounds. 2,2′-Biquinoline exhibits a much smaller dihedral angle between the two quinoline rings than does bipyridine or biphenyl.

The determination of the heat of combustion of solid substances leads to the determination of their heat of formation. This along with the heat of sublimation gives the gaseous heat of formation and heat of atomisation. Comparison of experimental and theoretical (based on bond energies) heats of atomisation yields the resonance stabilisation energies (r.s.e.). The replacement of a carbon with a heteroatom in hydrocarbons leads to interesting effects as far as r.s.e. is concerned. Thus in the series benzene, pyridine, pyridazine, pyrimidine, and pyrazine the r.s.e. decreases.[1]

In biphenyl interesting information about the dihedral angle between the two π-moieties can be derived by comparing the r.s.e. of the molecule with that of benzene. While biphenyl is known to be almost planar in the solid state,[2] electron diffraction data,[3] and gas-adsorption chromatography,[4] give an angle of 42° for the gas phase. Electron transmission spectroscopy was used to obtain the angle for methyl-substituted biphenyls.[5] The bond linking the two benzene rings possesses an energy of 383.11 kJ $mol^{-1}$ which places it higher than a C–C single bond but much lower than that of a double bond.[6a] The value of 407.9 kJ $mol^{-1}$ was obtained by Coleman and Pilcher.[6b] The non-planar configuration seems to retain partial resonance between the rings, avoiding at the same time steric hindrance of the hydrogens *ortho* to the connective carbons. The introduction of nitrogen in 2,2′-bipyridine is an added complication, as the repulsions between the electron pairs has to be taken into account. Nevertheless, a more planar structure (dihedral angle 21.5°) is obtained when theoretical and experimental dipole moments are correlated.[7–9] Dielectric constant measurements confirm this.[10] The nitrogen atoms, however, seem to prefer *trans*positioning to avoid electron-pair repulsions.[7–10]

In this work the heats of combustion and the derived heats of formation for 1,2,4-triazole, indazole, 2,2′-bipyridine, and 2,2′-biquinoline are reported. Resonance energies for these and related compounds are calculated and compared.

**Table 1.** Typical data

| | 2,2′-Bipyridine | 2,2′-Biquinoline | Indazole | 1,2,4-Triazole |
|---|---|---|---|---|
| $m'$(cpd.)/g | 0.887 47 | 0.952 77 | 0.732 69 | 0.989 76 |
| $\Delta T_{ad}$/K | 2.979 | 3.334 | 2.327 | 1.897 |
| $\varepsilon$/J $K^{-1}$ | 16.34 | 16.49 | 15.99 | 15.87 |
| $-\Delta U_{comb.}$/J | 30 139.2 | 33 731.4 | 23 542.0 | 19 191.5 |
| $\Delta U(HNO_3)$/J | 74.98 | 63.53 | 70.59 | 116.47 |
| $\Delta U_{\Sigma}$/J | 16.18 | 20.71 | 11.58 | 3.80 |
| $-m'''\Delta U_c°$(fuse) | 42.34 | 40.42 | 35.61 | 34.64 |
| $-\Delta U_c° M^{-1}$/J $g^{-1}$ | 33 810.5 | 35 272.8 | 31 970.1 | 19 233.5 |

Symbols: $m'$ = weight of compound; $\Delta T_{ad}$ = temperature rise during reaction. $\varepsilon$ = energy of mixing for final products; $\Delta U_{comb.}$ = experimental energy of combustion referred to final temperature; $\Delta U(HNO_3)$ = energy due to nitric acid formation and dilution; $\Delta U_{\Sigma}$ = Washburn correction; $m'''\Delta U_c°$(fuse) = energy due to combustion of fuse. $\Delta U_c°$ = standard energy of combustion at 298.15 K and 1 atm.

## Experimental

We have used the Parr 1241 adiabatic oxygen bomb calorimeter to determine the heats of combustion. Parr NBS certified benzoic acid was used to determine the energy equivalent of the calorimeter (the heat of combustion used for benzoic acid is 26.434 kJ $g^{-1}$ [11]). The energy equivalent determined by us was 10 100.9 J $K^{-1}$. This was the average of several runs. Monthly checks were made to comply with ASTM standards on reproducible energy equivalents.[12] Recommended starting conditions of 25 °C, initial temperature, a sample weight of 1 g and initial bomb pressure of 30 lb $in^{-2}$ were adhered to as closely as possible. Otherwise a suitable correction was made for deviations from ASTM conditions.[13] All chemicals were purchased from Fluka or Aldrich. Puriss or Gold label reagents were used without further purification. Otherwise 99% grade reagents were vacuum sublimed.

The actual experiment was run by using the Parr steel wire fuse with an energy of combustion equal to 2.3 cal $cm^{-1}$. The sample was pelleted, weighed, and placed in the sample crucible with the fuse wire touching its top. The sample holder was placed in a Parr oxygen bomb (containing 1 ml of distilled water) and the lid was tightly closed. The bomb was flushed three times and filled with oxygen at 30 lb $in^{-2}$. The bomb was lowered in the calorimeter bucket containing distilled water (2 l). The top of the calorimeter was closed and temperature equilibrium was allowed to occur. Temperature readings were taken after ignition. The instrument automatically took periodic pre-ignition temperature readings, ignited the fuse, and continued taking readings till temperature equilibrium was attained again. Meanwhile, hot water is automatically withdrawn into the jacket to keep the jacket and bucket at the same temperature all the time. This ensured adiabatic conditions during and after ignition. On completion of the experiment, the unburnt portion of the fuse was compared (by length or weight) to that of the original fuse to obtain the energy released by its combustion. The bomb washings were titrated with standard NaOH to determine the amount of acid formed ($HNO_2$ and $HNO_3$).

## Results and Discussion

Tables 1 and 2 give the experimental results showing typical data for each compound and the standard energy of combustion resulting from each run and the mean value [$\Delta U_c°/M$ (cpd)]. These results include the Washburn corrections. Table 3 gives the standard energy and enthalpy of combustion of the solid compounds [$\Delta U_c°$(c) and $\Delta H_c°$(c)]. The calculated standard

**Table 2.** $-\Delta U_c^{\circ}M(c)^{-1}/J\ g^{-1}$ at 298.15 K

| | 2,2′-Bipyridine | 2,2′-Biquinoline | Indazole | 1,2,4-Triazole |
|---|---|---|---|---|
| | 33 810.5 | 35 272.8 | 31 970.1 | 19 233.5 |
| | 33 863.7 | 35 294.3 | 32 024.9 | 19 280.3 |
| | 33 789.4 | 35 333.6 | 31 938.1 | 19 272.9 |
| | 33 803.5 | 35 247.5 | 31 980.9 | 19 277.0 |
| | 33 858.7 | 35 277.9 | 31 954.7 | 19 272.7 |
| | | 35 300.8 | | |
| Mean | 33 825.2<br>±30.2 | 35 287.8<br>±26.6 | 31 973.7<br>±29.4 | 19 267.3<br>±17.1 |

**Table 3.** Standard heats of sublimation and formation (kJ $mol^{-1}$)

| | $-\Delta U_c^{\circ}$(c) | $-\Delta H_c^{\circ}$(c) | $\Delta H_f^{\circ}$(c) | $\Delta H^{\circ}$(sub.)[a] | $\Delta H_f^{\circ}$(g) |
|---|---|---|---|---|---|
| 1,2,4-Triazole | 1 330.7 ± 1.2 | 1 328.9 ± 1.2 | 113.1 ± 1.4 | 80.62 ± 0.52 | 193.7 ± 1.9 |
| Indazole | 3 777.3 ± 3.5 | 3 778.6 ± 3.5 | 166.5 ± 3.7 | 87.74 ± 0.85 | 254.2 ± 4.6 |
| 2,2′-Bipyridine | 5 283.0 ± 4.7 | 5 285.5 ± 4.7 | 207.1 ± 4.9 | 81.93 ± 0.33 | 289.0 ± 5.2 |
| 2,2′-Biquinoline | 9 044.5 ± 6.8 | 9 049.4 ± 6.8 | 251.3 ± 7.0 | 96.55 ± 0.90 | 347.9 ± 7.9 |

[a] Ref. 14.

**Table 4.** Energies of atomisation and r.s.e. in kJ $mol^{-1}$

| | $\Delta H_f^{\circ}$(g) | $\Delta E_a^{\circ}$(g) | $\Delta E_a^{\circ}$(g, calc) | −R.s.e. |
|---|---|---|---|---|
| Cyclopentadiene[a] | 130.8 | 4 735.7 | 4 729.2 | 6.5 |
| Furan | 34.73[d] | 3 933.3 | 3 953.8 | −20.5 |
| Pyrrole | 108.38[d] | 4 298.7 | 4 204.7 | 94.0 |
| 1,2,4-Triazole | 193.7 | 3.294.3 | 3 218.2 | 76.1 |
| Indene | 163.5[d] | 7 990.8 | 7 845.0 | 145.8 |
| Indole | 186.6[d] | 7 508.2 | 7 322.8 | 185.4 |
| Indazole | 254.2 | 6 981.1 | 6 765.9 | 215.2 |
| Benzofuran[b] | 27.20 | 7 237.9 | 7 075.5 | 162.4 |
| Benzene[a] | 82.9 | 5 497.8 | 5 344.9 | 152.9 |
| Biphenyl[a] | 182.3 | 10 545.7 | 10 237.9 | 307.8 |
| Pyridine[a] | 140.2 | 4 981.0 | 4 857.4 | 123.6 |
| 2,2′-Bipyridine | 289.0 | 9 524.9 | 9 272.1 | 252.8 |
| Quinoline[c] | (8 232.2) | 8 192.6 | 7 975.5 | 217.1 |
| 2,2′-Biquinoline | 347.9 | 16 036.6 | 15 508.2 | 528.4 |

[a] Ref. 18*c*. [b] Ref. 19. [c] $\Delta H_a^{\circ}$(g) as given in ref. 20. [d] Ref. 21.

heat of formation [$\Delta H_f^{\circ}$(c)] along with the experimental heats of sublimation $\Delta H^{\circ}$(sub)[14] yield the gaseous standard heats of formation [$\Delta H_f^{\circ}$(g)]. The results for triazole agree very well with those of Aleksandrov and his co-workers.[15] Their energy of combustion is $-19\,211.3 \pm 13$ J $g^{-1}$ (a difference of 0.3% from ours) and yields $\Delta H_c^{\circ}$(c) $-1\,324.99 \pm 0.90$ kJ $mol^{-1}$ and $\Delta H_f^{\circ}$(c) $= 109.22 \pm 0.94$ kJ $mol^{-1}$. The heat of formation of indazole was calculated at 244.38 kJ $mol^{-1}$[16] as opposed to our experimental 254.2 kJ $mol^{-1}$.

To assess the effect of heteroatom substitution on resonance energies (r.s.e.), the latter were calculated as the difference between experimental gaseous energies of atomisation [$\Delta E_a^{\circ}$(g)] and calculated ones [$\Delta E_a^{\circ}$(calc)]. The experimental values, $\Delta E_a^{\circ}$(g), were calculated from $\Delta H_a^{\circ}$(g) which in turn were obtained from standard heats of formation of gaseous atoms C, H, N, and O[17] and our experimental gaseous heats of formation. In the calculation of $\Delta E_a^{\circ}$(calc), the use of bond energies alone is erroneous since this procedure ignores the contribution of bond–bond interactions to this quantity. Thus the Allen scheme,[18] using bond energy data available in refs. 17 and 18*c*, was employed. For the sake of comparison the resonance energies of similar compounds (as calculated in ref. 18*c* or by us from reported experimental data) are included. Table 4 lists the results and it is noteworthy that in the series furan, cyclopentadiene, 1,2,4-triazole, and pyrrole the resonance energy increases with furan possessing a (negative) destabilisation energy. This means that on the whole nitrogen substitution has a stabilising effect as compared with oxygen or $CH_2$ group in five-membered rings. In benzo-accumulated five-membered rings the nitrogen substitution again increases the r.s.e. (indazole > indole > indene). However, in benzofuran the r.s.e. is higher than the parent hydrocarbon indene. This latter conclusion however may be erroneous since our calculation of r.s.e. of benzofuran is not based on experimental heat of formation but rather on a theoretical estimate.[19] The trend we obtain still compares well with that of the Dewar resonance energies for indene, indole, and benzofuran (72, 99.6 and 84.9 kJ $mol^{-1}$[22–24] respectively). A similar trend for N and O benzo-five-membered rings was calculated.[25]

The resonance energies of biphenyl, 2,2′-bipyridine, and 2,2′-biquinoline are very indicative of the nature of the connective bond between the two ring systems. A fully planar molecule (dihedral angle = 0 or 180° for *trans*-nitrogens) would lead to highest resonance. In this case delocalisation occurs over both ring systems and the connective bond would be close in double bond character to those in the ring. A 90° configuration would lead to a resonance energy which is twice that of the parent molecule. In all three cases the resonance energies obtained are higher than expected for the 90° configuration. In bipyridine the increased stabilisation is higher than in biphenyl thus confirming the smaller dihedral angle in 2,2′-bipyridine (with nitrogen atoms *trans* to each other).[3,4,7–9] In 2,2′-biquinoline the additional stabilisation is even higher. Following reactions (1)—(3) and using the tabulated $\Delta H_f^{\circ}$(g), one calculates the

$$\text{biphenyl} + H_2 \longrightarrow 2\ C_6H_6\ \text{(benzene)} \tag{1}$$

$$\text{2,2}'\text{-bipyridine} + H_2 \longrightarrow 2\ C_5H_5N\ \text{(pyridine)} \tag{2}$$

$$\text{2,2}'\text{-biquinoline} + H_2 \longrightarrow 2\ C_9H_7N\ \text{(quinoline)} \tag{3}$$

reaction enthalpy, $\Delta H_{rxn}^{\circ} = -16.50, -8.60$, and 85.05 kJ $mol^{-1}$ respectively. The above reactions involve breaking the connective C–C bond, the H–H bond, and the formation of 2 C–H bonds. Using the proper H–H and C–H bond energies[17,18] leads to the connective C–C bond energies of 374.16, 382.06, and 475.7 kJ $mol^{-1}$, respectively, with the expected increase in double bond character: biphenyl < 2,2′-bipyridine < 2,2′-biquinoline.

## Acknowledgements

We thank Yarmouk University, Irbid, for financial support. We are greatly indebted to Dr. G. Pilcher, Professor H. A. Skinner, and Dr. G. Al-Takhin, Chemistry Department, University of Manchester, for measuring the heats of sublimation and for the use of their minicomputer facility to calculate the Washburn corrections.[26] Stimulating discussions with Dr. Pilcher were also very helpful.

## References

1 J. Tjebbes, *Acta Chem. Scand.*, 1962, **16**, 916.
2 A. Hargreaves and S. H. Rizui, *Acta Crystallogr.*, 1962, **15**, 365; J. Trotter, *ibid.*, 1961, **14**, 1135.

3 A. Almenningen and O. Bastiansen, *Det. Kgl. Norske Vidensk. Selskabs Skrifter*, 1958, **4**.

4 A. J. Grumadas and D. P. Poshkus, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 2013.

5 G. Distefano and D. Jones, *Chem. Phys.*, 1983, **82**, 489.

6 (*a*) R. Sabbah and P. Laffitte, *C. R. Acad. Sci. Paris*, 1979, **289C**, 153; (*b*) D. J. Coleman and G. Pilcher, *Trans. Faraday Soc.*, 1966, **62**, 821.

7 A. B. Bolotin, V. A. Bolotin, and V. L. Gineityte, *Int. J. Quant. Chem.*, 1979, **16**, 839.

8 C. W. N. Cumper, R. F. A. Ginman, and A. I. Vogel, *J. Chem. Soc.*, 1962, 1188.

9 P. H. Cureton, C. G. Le Févre, and R. J. W. Le Févre, *J. Chem. Soc.*, 1963, 1736.

10 P. Freudlich, E. Jakusk, H. A. Kolodziej, A. Koll, M. Pajdowska, and S. Sorriso, *Z. Phys. Chem.* (*Wiesbaden*), 1982, **131**, 161.

11 ASTM Standards, ANSI/ASTM D 240–76, method 2502-Federal Test Method Standard No. 791b, 1976.

12 ASTM Standards, ANSI/ASTM D 2015–66 (reapproved 1972), 1972.

13 ASTM Standards, ANSI/ASTM D 2382 (76), Federal Test Method Standard 791b, 1976.

14 H. A. Skinner, G. Pilcher, and G. Al-Takhin, personal communication.

15 Y. I. Alexandrov, T. P. Okunova, and B. F. Yukevich, *Termodin. Org. Soedin.*, 1982, 42.

16 G. Lewis, *Corrosion*, 1984, **38**, 60.

17 CODATA, *J. Chem. Thermodynam.*, 1978, **10**, 903.

18 (*a*) T. L. Allen, *J. Chem. Phys.*, 1959, **31**, 1039; (*b*) H. A. Skinner, *J. Chem. Soc.*, 1962, 4396; (*c*) H. A. Skinner, 'Thermochemistry of Molecules, Molecule-Ions and Free Radicals. Factors Influencing Bond Energies is in these Species' in M. A. V. Ribeiro da Silva (ed.), 'Thermochemistry and its Applications to Chemical and Biochemical Systems,' Riedel, Amsterdam, 1984, p. 569.

19 (*a*) S. E. Stein and B. D. Barton, *Thermochim. Acta*, 1981, **44**, 265; (*b*) M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, 1966, **44**, 759.

20 M. J. S. Dewar and T. Morita, *J. Am. Chem. Soc.*, 1969, **91**, 796.

21 J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

22 M. H. Palmer and S. M. F. Kennedy, *J. Chem Soc., Perkin Trans. 2*, 1976, 81.

23 M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, *Tetrahedron*, 1970, **26**, 4505.

24 B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, 1972, **28**, 3657.

25 A. Mehlhorn and J. Fabian, *Croat. Chem. Acta*, 1981, **54**, 427.

26 Washburn Corrections were made according to the procedure described in M. Mansson and W. N. Hubbard in 'Experimental Chemical Thermodynamics—Combustion Calorimetry,' eds. S. Sunner and M. Mansson, Pergamon, Oxford, 1979, vol. 1, ch. 5, W. N. Hubbard, D. W. Scott, and G. Waddington in 'Experimental Thermochemistry,' ed. F. D. Rossini, Interscience, New York, 1956, vol. 1, ch. 5.

*Received* 23rd *July* 1984; *Paper* 4/1260