Thermochimica Acta, 34 (1979) 383—385

Note

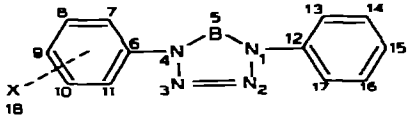
HEAT OF ATOMIZATION OF UNSYMMETRICALLY *N*-SUBSTITUTED Δ^2-TETRAZABOROLINES USING IOC-ω TECHNIQUES

D.C. RAJWAR and S.C. TIWARI

Department of Chemistry, K.N. Government Postgraduate College, Gyanpur (Varanasi) (India)

(Received 2 March 1979)

The IOC-ω technique has been found to be a convenient method for calculating the heat of formation of organic compounds [2—4]. We have previously [5,6] calculated the heat of formation of some cyclazines and benzanthrone, acedianthrone and flavanthrone using this technique. Leach et al. [1] have synthesised stable Δ^2-tetrazaborolines (I) and carried out molec-



(I)

ular orbital calculations by the modified Huckel approach. Using their data of π-bond orders and atomic charges, we are able to calculate the heat of atomization of these compounds using the IOC-ω technique.

METHOD OF CALCULATION

Details of the IOC-ω technique have been described in the literature [2—4]. The expression for the total π-electron energy by this method may be given as

$$E_\pi = \sum_r q_r\alpha_r + \omega \sum_r q_r(1 - q_r) - \omega_s \sum_{j \neq r} \sum_r q_r p_{rj} + 2\beta \sum_{r<s} \sum p_{rs} \quad (1)$$

The energy liberated ($E_{\pi b}$) when n atoms combine with p-electrons to form a π bond

$$E_{\pi b} = -[\omega \sum_r q_r(1 - q_r) - \omega_s \sum_{j \neq r} \sum q_r p_{rj} + 2\beta \sum_{r<s} \sum p_{rs}] \quad (2)$$

where q_r is the electronic charge at an atom r; p_{rs} is the bond-order between atoms r and s, and ω is an empirical parameter assigned the values ranging from 0.33 to 1.8 in the literature [7]. In the present calculation a value of 1.3 for this parameter gives the best results. The empirically adjusted parameter β has been assigned a value of 1.5. The heat of atomization of an organic compound is equal to the sum of the total π-bond and σ-bond energies (eqn. (3)).

$$-\Delta H_a = E_{\pi b} + E_{\sigma b} \quad (3)$$

The σ-bond energy ($E_{\sigma b}$) can be calculated by the expression

$$E_{\sigma b} = \sum N_x E_x \quad (4)$$

where x represents the atoms present (including carbon and hydrogen) in the given compound, N_x is the number of C—C, C—H, C—N, C—Cl, B—N and N—N bonds and E_x is their corresponding bond energies. In our previous calculations [5,6] only the bonds attached to carbon atoms were considered, but in the present calculation we have also considered the bonds of the type B—N and N—N in which boron and nitrogen atoms are present in π lattices. The values of the bond energies for C—H, C—N and C—Cl bonds equal to 4.43, 2.9 and 3.41 eV, respectively, are well established [8]. The C—C bond energy E_c has been empirically adjusted to 3.7 eV which is very close to the value of 3.80 eV used by Dewar and Gleicher [9]. The π-bond energies [10] for B—N and B—H bonds have been taken as 4.61 and 4.03 eV, respectively.

RESULTS

The calculated values of heat of atomization of all the compounds using eqns. (2, 3 and 4) are presented in Table 1. Since the data for the heat of atomization of Δ^2-tetrazaborolines are not available in the literature, an indirect procedure has been adopted to confirm eqns. (1 and 2), the expression for total π-electron energy may be written as

$$E_\pi = \sum q_r \alpha_r + E_{\pi b} \quad (5)$$

where for a particular compound all carbon α-values were set equal. The α_r-values were expressed by

$$\alpha_r = \alpha_r^0 + (1 - q_r)\beta_{c-c} \quad (6)$$

in which $\omega = 1.3$ for all cases and β_{c-c} was taken as -3.16 [1]. Initially the

TABLE 1

Calculated π-electron energies and heat of atomization ($\beta = -3.116$ eV)

Compound	$E\pi$ (β units, eV)		ΔH_a (eV)
	Calc.	Leack et al [1]	
$(C_6H_5)_2N_4BH$	28.967	29 016	131.292
(o-ClC_6H_4)(C_6H_5)N_4BH	29.049	29.056	127 882
(m-ClC_6H_4)(C_6H_5)N_4BH	29.051	29.056	127.877
(p-ClC_6H_4)(C_6H_5)N_4BH	29.060	29 056	127 849
(o-MeC_6H_4)(C_6H_5)N_4BH	35.162	35 191	141 694
(m-MeC_6H_4)(C_6H_5)N_4BH	35.161	35 192	141.690
(p-MeC_6H_4)(C_6H_5)N_4BH	35.150	35.191	141.735

α_r^0 were given the values [11]

$$\alpha_r^0 = \alpha_{c-c} + h\beta_{c-c} \quad (7)$$

where $h = -1, 2, 1, 2, 3$ for r = boron, nitrogen bonded to a substituent, azonitrogen, chloro and methyl, respectively. The values of α_r are empirically adjusted, and are assigned the values —7.12, —6.7 and —7.67 eV for unsubstituted, chloro- and methyl-substituted hetero-atoms, respectively. Thus, substituting the calculated values of $\Sigma q_r \alpha_r$ and $E_{\pi b}$ in eqn. (5), total π-electron energy E_π is evaluated (Table 1).

The results obtained clearly demonstrate successful application of the IOC-ω technique for calculating the heat of atomization of substituted Δ^2-tetrazaborolines. The present calculation also supports the values of π-bond orders and π-electron-charge densities calculated by Morris and co-workers [1].

ACKNOWLEDGEMENTS

The authors are thankful to Dr. S.S. Khanna, Principal, and Professor Baquaridi, Head of Chemistry Department, for providing the research facilities. One of the authors (D.C.R.) is thankful to Dr. S.C. Tiwari for his criticism and suggestions.

REFERENCES

1 J B. Leach, J.H Morris and P G Perkins, J. Chem Soc. A, (1970) 1077
2 B. Krishna and S P. Gupta, J. Chem. Soc. A, (1970) 917.
3 B. Krishna and S.P. Gupta, J. Am Chem Soc., 92 (1970) 7247.
4 S. Sharma and B. Krishna, Indian J. Chem , 14A (1976) 435
5 S.C. Tiwari, Indian J. Chem., (1977) 238.
6 D.C. Rajwar and S.C Tiwari, Curr. Sci., 47 (1978) 376.
7 A Streitwieser, Jr. and P.M. Nair, Tetrahedron, 5 (1959) 149; N. Muller, L W. Pickett and R.S. Mulliken, J. Am. Chem. Soc , 76 (1954) 4770
8 L N. Ferguson, The Modern Structural Theory of Organic Chemistry, Prentice-Hall of India, New Delhi, 1969, p 48.
9 M.J.S Dewar and G. Gleicher, J. Chem. Phys , 44 (1969) 759.
10 Advances in Inorganic and Radio Chemistry, Vol 5, Academic Press, New York, (1963), pp. 259—300.
11 J H. Morris and P G. Perkins, J. Chem Soc. A, (1966) 576