

## Ionization potentials and heats of formation of some non-benzenoid hydrocarbons and heterocyclic molecules

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An improved IOC- $\omega$  technique discussed in previous papers of this series has been further extended to oxygen containing compounds, aromatic amines and to nitrogen containing compounds in which nitrogen atom contributes two  $\pi$  electrons to the system. The values of  $\pi$ -bond energies and heats of formation of these molecules have been calculated and the success of the technique is again supported by the comparison of calculated and experimental values. The technique has also been employed on non-benzenoids to calculate their ionization potentials and heats of formation and the results have been compared with those obtained by s. c. f. methods.

### 1. INTRODUCTION

In previous papers (Sharma *et al.*, 1975, 1976) of this series, we have discussed in detail an improved IOC- $\omega$  technique and obtained encouraging results for various properties (e.g., ionization potentials, electron affinities,  $\pi$ -bond energies, heats of formation and resonance energies) of alternant and non-alternant hydrocarbons and nitrogen containing heterocyclic molecules in which hetero atom contributes one electron to the system. This inspired us to apply the same method to non-benzenoid hydrocarbons such as Hafner's hydrocarbons (aceazulylene and aceheptylene), pyracetylene, di-pleiapentalene, iso-pyrene and azulenoheptalene and nitrogen and oxygen containing molecules and aromatic amines and to compare the results with those obtained by s.c.f. methods. In the present communication, we have restricted our discussion to non-benzenoid hydrocarbons with five or seven membered rings.

In the present method we have used the following matrix elements (eqn. 1 : Krishna & Gupta, 1970; eqn. 2 : Boyd & Singer, 1966) and the method of calculation has already been discussed in detail in previous papers (Sharma *et al.* 1975, 1976) and hence is not repeated here.

$$H_{rr} = \alpha_r + \omega \left[ 1 - \frac{1}{2} \sum_j (P_{rj}S_{rj} + P_{jr}S_{jr}) \right] \quad (1)$$

$$H_{rs} = \beta_0 \exp.(0.55 P_{rs} - 0.3666). \quad (2)$$

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## 2. CHOICE OF THE PARAMETERS

When a molecule is derived from a conjugated hydrocarbon by the introduction of a hetero atom, it is no longer reasonable to take all  $\alpha$ 's equal for atoms of conjugated system. A hetero atom ought to be characterized by a parameter  $\alpha$  different from that of a carbon atom. It might also be expected that resonance integral,  $H_{rs}$  between a hetero atom and a neighbouring carbon atom would be different from the resonance integral which characterizes a pair of carbon atoms.

According to Wheland & Pauling (1935) these changes in the values of  $\alpha$  and  $\beta$  can be incorporated in units of standard  $\alpha_c$  and  $\beta_{cc}$ , usually of benzene, by the use of the definitions :

$$\alpha_X = \alpha_C + h_X \beta_{CC} \quad \dots (3)$$

$$\beta_{CX} = K_{CX} \beta_{CC} \quad \dots (4)$$

Here  $X$  represents the hetero atom.

When nitrogen atom is contributing two electrons to the  $\pi$ -system, these  $h$  and  $K$  parameters will certainly differ from parameters earlier taken for nitrogen atoms contributing one electron to the  $\pi$ -system. For aromatic amines and nitrogen containing molecules we have taken,  $h = 1$ , and  $K = 1$ , in this work, which are very close to generally used values (Matsen, 1950; Srivastava & Krishna, 1973). However, less consistency has been shown for the oxygen parameters. The following values which have been found suitable for approximate work by many workers (Kuboyama *et al*, 1954, 1958) have been used.

$$h_o = 1, h_o = 2 \text{ and } K_{CO} = 1.$$

In the calculations, we have used,  $\alpha = -8.45$  eV, which is however, very close to the value suggested by Jug (1970).  $\beta_0$  has been taken as  $-2.39$  eV as used by Pariser & Parr (1953). Overlap integral  $S$ , as usual has been taken as 0.25 and  $\omega$  has been assigned a value  $-5.43$ . These are the exactly similar as ones used in our previous papers (Sharma *et al* 1975, 1976).  $\alpha$  for hetero atom,  $\alpha_X$  has been calculated with the help of eq. (3). The values of various bond energy terms required for the evaluation of heats of formation are those obtained by Dewar & Gleicher (1966) from heats of formation measurements.

## 3. HEATS OF FORMATION OF HETEROCYCLIC MOLECULES

The results of our calculations using an improved IOC- $\omega$  technique for the calculation of heats of formation of aromatic amines and nitrogen and oxygen containing heterocyclic molecules have been reported in table 1. The results are seen to correlate very well with the experimental value (Dewar, 1969) and

Table 1. Heats of formation of some nitrogen and oxygen containing molecules

Molecule	$\pi$ -Bond energy $E_{\pi b}$ , eV	Heat of formation, eV			
		This work	Dewar and Hargot (1970)	Dewar and Morita (1969)	Experimental values (Dewar, (1969)
Pyrrole	5.715	46.330	44.40	44.47	44.94
Indole	11.137	78.507	78.16	78.44	78.39
Iso-Indole	10.904	78.271	—	—	—
Carbazole	16.040	111.345	111.99	112.18	111.91
Aniline	8.366	64.604	64.37	64.39	64.31
$\beta$ -Naphthylamino	13.812	97.305	97.82	97.81	98.78
Benzofuran	10.359	75.030	75.34	75.38	—
Dibenzo-furan	16.442	109.048	109.19	109.22	109.18
$\alpha$ -Naphthol	13.546	94.868	95.04	95.12	—
$\beta$ -Naphthol	14.424	95.746	95.04	95.12	—
Benzaldehyde	8.365	68.906	68.27	68.51	68.27

are almost as good as obtained by Dewar *et al* (1969, 1970) using an improved s.c.f. treatment, except in the case of pyrrole.

#### 4. HEATS OF FORMATION OF NON-BENZENOID HYDROCARBONS

Recently Das Gupta & Das Gupta (1972) and Birss & Das Gupta (1971) have reported the results of their calculations on some non-benzenoid and semi-benzenoid molecules, giving their  $\pi$  and  $\sigma$  bond energies, heats of atomization and resonance stabilization energies and studied their aromaticity. We list their values in table 2, designated as s.c.f. (a) and s.c.f., (b), for comparison with our calculated values of heats of formation. The two s.c.f. methods differ only in way of calculation of resonance integrals. In the first method named as s.c.f. (a), a value dependent on bond lengths as proposed by Lo & Whitehead (1968) was used, while in the second method, s.c.f. (b), a constant value of  $\beta$ ,  $-1.7901$  eV determined by the method of Chung & Dewar (1965). The values obtained by Das Gupta *et al* (1971, 1972) are in excellent agreement with our calculated values. Thus we conclude that results obtained by present method are equally competent to a modified PPP methods (1971, 1972) which involve many of the two electron repulsion integrals, which have been previously neglected by Heilbronner & Co-workers (1965) for calculations on these molecules.

Table 2. Calculated heats of formation of some non-benzenoid hydrocarbon

Molecule	$\pi$ -bond energy, $E_{\pi b}$ , eV	Heat of formation, eV		
		Present work	SCF (a)	SCF (b)
Accepleadiylene	20.369	137.172	138.043	136.787
Pyraoheptylene	19.913	136.716	137.090	136.463
Diploiapentalene	20.046	136.849	136.895	136.860
Diploiadadrene	23.475	156.777	155.924	156.110
Acoazulylene	14.641	103.509	104.021	103.596
Accheptylene	17.390	122.657	122.896	121.935
Azulonoheptalene	21.994	155.296	155.493	155.675
Isopyrene	19.246	136.049	136.404	136.371
Ploiadione	18.393	123.760	123.212	123.440
Benzoploiadione	23.314	156.616	156.142	156.421
Naphthoazulene	20.624	137.427	137.667	137.125

## 5. IONIZATION POTENTIALS OF NON-BENZENOID HYDROCARBONS

Table 3 reports ionization potentials of some semi-benzenoid and non-benzenoid hydrocarbons calculated by present method and three s.c.f. methods

Table 3. Ionization Potentials of Non-benzenoid Hydrocarbons

Molecule	Ionization Potential, Present work, eV	Ionization Potential, eV					
		Uncorrected			Corrected		
		S.C.F. (a)	S.C.F. (b)	S.C.F. (c)	S.C.F. (a)	S.C.F. (b)	S.C.F. (c)
Acoazulylene	7.02	9.36	9.23	9.38	8.03	7.90	7.49
Accheptylene	6.98	8.86	8.58	8.85	7.53	7.25	6.94
Pyraoheptylene	7.18	8.75	8.82	8.72	7.42	7.49	7.15
Diploiapentalene	7.85	9.10	8.95	9.19	7.77	7.62	7.40
Isopyrene	6.50	7.82	7.90	8.02	6.49	6.57	6.38
Azulonoheptalene	6.79	8.28	8.31	8.46	6.95	6.98	6.65
Accepleadiylene	7.56	9.14	8.94	—	—	7.61	—
Naphthoazulene	7.28	8.92	8.75	—	—	7.42	—

(a) Correction made according to Bloor's formula.

(b) Correction made according to Kuni and Kuroda's formula.

(Das Gupta *et al* 1971, 1974; Dewar & Harget, 1970). The two methods, s.c.f. (a) and s.c.f. (b) have already been described. The remaining method, s.c.f. (c) is due to Dewar & Harget (1970).

It has commonly been observed (Moser, 1955) that the values of ionization potentials obtained by Koopman's theorem (1934) using s.c.f. methods are 1 to 2 eV too high. Hoyland & Goodman (1960) have shown this discrepancy can be accounted for by  $\sigma$  core contraction and  $\pi$ -orbital deformation in the ionized molecule. In context of the constant  $\beta$  calculations s.c.f. (b) Bloor (1965) has proposed a general corrected ionization energy for hydrocarbons as  $-(\epsilon_h + 1.33)$  eV, where  $\epsilon_h$  is the highest occupied molecular orbital energy. For " $\beta$  variable" method ionization energy is given by the following equation proposed by Kuni & Kuroda (1968)

$$I = -(\epsilon_h + 1.06)$$

$\epsilon_h$  is as defined above.

The table 3 also contains the values of ionization potentials corrected by Bloor's (1965) method and Kuni & Kuroda's (1968) formula. It is amply clear that our calculated values are much closer to corrected ionization potentials than the uncorrected values.

The work reported here seems to suggest that our treatment can be extended to the systems containing hetero atoms which contribute two  $\pi$  electrons, with the results of sufficient accuracy to be useful for chemical purposes.

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#### REFERENCES

- Baugartner P., Weltin E., Wagniere G., & Heilbronner E. 1965 *Helv. Chim. Acta*, **48**, 751.  
Birss F. W. & Das Gupta N. K. 1971 *Canadian J. Chem.*, **49**, 2840.  
Bloor J. E. 1965 *Canadian J. Chem.*, **43**, 3026.  
Boyd G. V. & Singer N. 1966 *Tetrahedron*, **22**, 3383.  
Chung A. L. H. & Dewar M. J. S. 1965 *J. Chem. Phys.* **42**, 756.  
Das Gupta A. & Das Gupta N. K., 1972 *Tetrahedron*, **28**, 3587.  
Das Gupta A. & Das Gupta N. K., 1974 *Canadian J. Chem.*, **52**, 155.  
Dewar M. J. S. 1969 *The Molecular Orbital Theory of Organic Chemistry* McGraw-Hill Book Co., Inc., New York, 378, 382.  
Dewar M. J. S. & Gleicher G. J., 1966 *J. Chem. Phys.*, **44**, 759.  
Dewar M. J. S. & Harget A. J., 1970 *Proc. Roy. Soc.*, **A315**, 457.  
Dewar M. J. S. & Morita T., 1969 *J. Amer. Chem. Soc.*, **91**, 796.  
Hoyland J. R. & Goodman L., 1960 *J. Chem. Phys.*, **33**, 946.

- Jug K., 1970 *Theoret. Chim. Acta*, **16**, 95.  
Koopmans T., 1934 *Physics*, **1**, 104.  
Krishna B. & Gupta S. P., 1970 *J. Amer. Chem. Soc.* **92**, 7247.  
Kuboyama A., 1958 *Bull. Chem. Soc. Japan*, **31**, 752.  
Kuni T. L. & Kuroda H., 1968 *Theoret. Chim. Acta*, **11**, 97.  
Lo D. H. & Whitehead M. A. 1968 *Canadian J. Chem.* **46**, 2027.  
Matsen F. A., 1950 *J. Amer. Chem. Soc.*, **72**, 5243.  
Moser C., 1955 *J. Chim. Phys.*, **52**, 24.  
Nagakura S. & Kuboyama A., 1954 *J. Amer. Chem. Soc.*, **76**, 1003.  
Parisor R. & Parr R. G., 1953 *J. Chem. Phys.* **21**, 466, 767.  
Sharma S. C. & Krishna B., 1976 *Ind. J. Chem.*, **14A**, 435.  
Sharma S. C. & Krishna B., 1976 *Indian J. Phys.*, **50**, 406.  
Sharma S. C., Srivastava A. K. & Krishna B. 1975 *J. Chem. Soc. Faraday Trans. II* **71**, 168,  
172  
Srivastava A. K. & Krishna B., 1973 *Indian J. Pure Appl. Phys.*, **11**, 354.  
Wheland G. W. & Pauling L., 1935 *J. Amer. Chem. Soc.* **57**, 2086.