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Resonance Energies of Some Compounds Containing Nitrogen or Oxygen*

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Resonance energies are calculated for a number of aromatic, and potentially aromatic, compounds containing nitrogen or oxygen, using a recent version of our SCF MO π approximation.

Recently we reported [1] a variant of our earlier SCF MO π approximation [2–5] in which the one-electron resonance integral (β^{C}_{ij}) is determined from the Mulliken relation instead of the Dewar-Schmeising thermocycle [6, 7]; i.e.

$$\beta^{\mathrm{C}}_{ij} = KS_{ij} \tag{1}$$

where K is a constant characteristic of the atoms i and j. This procedure avoids a difficulty inherent in the earlier treatment, i.e. the need for data concerning "pure" double bonds. Such data are available only for bonds formed by carbon, nitrogen, and oxygen; the thermocycle approach could not therefore be extended to other elements.

One important conclusion from the earlier papers was that bonds in classical polyenes [3, 4], and in classical conjugated compounds containing nitrogen or oxygen [8], are localized, in the sense that the calculated heats of atomization can be expressed as sums of "polyene" bond energies that carry over from one molecule to another. This led to a simple definition of resonance energy as the difference between the heat of atomization of a given compound, and that calculated for a corresponding classical structure using the "polyene" bond energies. This relation was also shown [1] to hold for hydrocarbons in the new approximation; here we report a further extension to compounds containing nitrogen or oxygen.

The appropriate "polyene" bond energies were found in exactly the same way as for the thermocycle approximation [4, 8]; the two sets of values are compared in Table 1. Heats of atomization were then calculated by the new procedure [1] for a number of conjugated compounds containing nitrogen or

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Table 1. *"Polyene" bond energies*

Bond	Bond energy (eV)	
	This paper	Refs. [4] and [8]
C–C	4.3860	4.3499
C=C	5.4648	5.5378
C–H	4.4375	4.4375
C–N[a]	3.7794	3.8343
C=N[a]	5.2120	5.1654
C–$\ddot{\text{N}}$[b]	3.5061	3.5903
$\ddot{\text{N}}$–H	4.0925	4.0418
C–$\ddot{\text{O}}$	4.1490	4.1594
C=O	6.7442	7.1575
$\ddot{\text{O}}$–H	4.7600	4.7700

[a] Pyridine-type nitrogen.

[b] Pyrrole-type nitrogen.

oxygen and their resonance energies deduced by comparison of the calculated heat of atomization with that estimated for a classical structure, using the bond energies of Table 1. Tables 2 and 3 list the calculated heats of atomization, together with experimental values where these are available, and the derived resonance energies.

The resonance energies predicted for amino, hydroxy, or carbonyl derivatives of hydrocarbons (aniline, phenol, benzophenone, naphthylamine, etc.) are almost identical with those of the hydrocarbons themselves (benzene, 22.6 kcal/mole; naphthalene, 33.6 kcal/mole [1]); this agrees with the conclusion [8] that the CO and CN bonds in phenols and amines, and the C–C(O) bonds in aromatic aldehydes and ketones, are "localized" in our sense of the term [4, 8].

The resonance energies predicted for azines are close to those of the isoconjugate hydrocarbons (cf. pyridine and pyrazine with benzene); this is also in agreement with the earlier treatment [8] and with the available chemical evidence. The resonance energies of the five-membered aromatics are likewise again predicted to be small (pyrrole, furan).

Several compounds are predicted to have negative resonance energies; here again the chemical evidence seems to be consistent with the prediction. Thus even derivatives of azete are difficult to prepare and are very reactive [9, 10], while 2-azirine and oxirene are still unknown [11]. Cyclopentadienone ($E_R = -5.3$ kcal/mole) has been obtained only as an extremely reactive intermediate which cannot be isolated since it dimerizes so readily [12]; note that the isoconjugate hydrocarbon, fulvene, for which $E_R = 1.1$ kcal/mole, is relatively stable [13–15]. Similar remarks apply to cyclopropenone ($E_R = -3.0$ kcal/mole) which has only recently been prepared and resisted all attempts to isolate it from solution because it polymerized so readily [16]; cyclopropenone bears the same relation to the aromatic ion, cyclopropenium, that tropone does to tropylium, and it had been suggested that it might, like tropone, be aromatic. It has, however, become increasingly evident that tropone is *not* an aromatic compound, a conclusion confirmed by calculations which will be reported elsewhere [17].

Table 2. *Heats of atomization (ΔH_a) and resonance energies (E_R) of nitrogen compounds*

Molecule	$-\Delta H_a$(exp.) (eV)	$-\Delta H_a$(calc.) (eV)	E_R(kcal/mole)
2-azirine		25.15	− 6.7
azete		34.18	−15.5
pyrrole	44.51[a]	44.40	5.3
aniline	64.31[b]	64.37	21.7
α-naphthylamine	97.79[c]	97.82	33.0
β-naphthylamine	97.78[c]	97.82	33.0
diphenylamine	116.53[c]	116.47	43.6
pyridine	51.79[d]	51.88	23.1
quinoline	85.18[c]	85.32	34.1
isoquinoline		85.32	34.1
pyrazine	46.44[e]	46.32	17.1
quinoxaline		79.76	28.1
1,5-naphthyridine		79.98	33.2
1,8-naphthyridine		80.12	36.4
acridine		118.60	41.3
pyrrocoline		76.90	6.9
2,2′-pyrrolylpyridine		91.77	27.9
2-aminopyridine		59.14	23.2
4-aminopyridine		59.13	22.9
1-aminoisoquinoline		92.59	34.5
3-aminoisoquinoline		92.57	34.0

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Table 3. *Heats of atomization (ΔH_a) and resonance energies (E_R) of oxygen compounds*

Molecule	$-\Delta H_a$(exp.) (eV)	$-\Delta H_a$(calc.) (eV)	E_R(kcal/mole)
oxirene		22.37	− 5.5
cyclopropenone		29.73	− 3.0
cyclopentadienone		48.35	− 5.3
furan	41.52[a]	41.56	4.3
diphenylether	113.84[b]	113.68	43.8
benzaldehyde	68.27[b]	68.27	22.1
α-naphthylaldehyde		101.72	33.4
β-naphthylaldehyde		101.73	33.7
phenol	61.60[c]	61.60	21.9
α-naphthol		95.04	33.0
β-naphthol		95.04	33.0
benzophenone	120.98[a]	120.87	43.1

[a] Wheland, G. W.: Resonance in organic chemistry. New York: Wiley 1955.
[b] Benson, S. W.: J. chem. Educ. **1965**, 502.
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