

479. *The Molecular-orbital Treatment of Organic Compounds containing Oxygen.*

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It is shown that the method of molecular orbitals gives reasonable values for the resonance energy of a variety of conjugated systems involving oxygen, provided that an adjustment to the Coulombic term of the oxygen atom is made. An interesting result is that this adjustment has little effect on the magnitude of the additional resonance energy calculated for vinylfuran and the furfuryl radical. It is further pointed out that, in the related hydrocarbon $R\cdot CH=CH_2$ and group $R\cdot CH_2$, the additional resonance energy, calculated by the molecular-orbital method, is not only little dependent on the resonance energy of the group R, whether it be aliphatic or cyclic in character, but is also similar to that of the furan compounds.

Some cyclic nitrogen compounds are also considered.

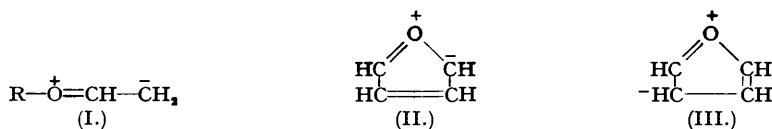
MOLECULAR-ORBITAL calculations overestimate the resonance energy of oxygen-containing compounds if no allowance is made for the greater electron affinity of the oxygen atom compared with carbon (cf. Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, 57, 2091). When this effect is ignored, the localisation of electrons on the oxygen atom is neglected and hence the derived binding energy is too large. Thus simple molecular-orbital treatment gives 2.48 β for the resonance energy of furan and 1.46 β for divinyl ether, compared with the empirical values of about 1 β and 0.2 β , respectively (where β , the C-C resonance integral, is considered to be 18 kcal.). It is the object of this paper to examine the molecular-orbital treatment of oxygen-containing compounds with the aim of establishing the simplest modification necessary to allow for the disturbing effect of the oxygen atom. The compounds treated include furan and pyran derivatives, vinyl ethers, and phenol, as well as the furfuryl radical.

The calculations were carried through in the usual manner and therefore require no detailed description. The π electron energy is expressed only in terms of the β component. The empirical resonance energies used for comparison were derived from heats of hydrogenation or heats of combustion (cf. Wheland, "The Theory of Resonance," John Wiley & Sons, 1944). For furan, a group method of estimation was also used (Bremner and Thomas, *Trans. Faraday Soc.*, 1948, 44, 230, 338).

Comparison of Suggested Methods.—Three modifications to the simple molecular-orbital treatment were considered. The first modification attempts to allow for the localisation effect by arbitrarily reducing the number of electrons. The second is based on a suggestion by Wheland (*op. cit.*, p. 52) that only structures with adjacent formal charges are significant. The third allows for the electro-negativity of the oxygen atom by adjustment of the parameters used in the molecular-orbital calculations (cf. Wheland and Pauling, *loc. cit.*; Evans, Gergely, and de Heer, *Trans. Faraday Soc.*, 1949, 45, 312).

(i) *Reduction in the number of π electrons.* Initially, it seemed feasible to allow arbitrarily for the electron affinity of the oxygen atom by working with less than the normal number of electrons used in the simple molecular-orbital treatment. By this means the binding energy of the molecule and consequently its resonance energy would be reduced, as is required. Furan seemed to respond well to this method of approach if two of the six π electrons were disregarded in the calculation. As the two lowest roots of the relevant secular equation are -2β and -0.62β , the π -electron energy now becomes 4.24 β , and consequently the resonance energy—referred to two C-C double bonds—is 1.24 β . This figure is in good agreement with the empirical values 0.95 β , 1.13 β , and 1.28 β derived from heats of hydrogenation, group calculations, and heats of combustion, respectively. However, this method of approach could be of value only if the correction for the localisation of electrons on the oxygen atom was of a general nature. Further consideration showed that this did not hold. Thus for vinyl ether the second orbital, and for phenol the fourth orbital, is neither bonding nor anti-bonding (*i.e.*, $W = 0$) and, in consequence, a reduction by two in the number of electrons now leaves unchanged the derived resonance energy in both instances.

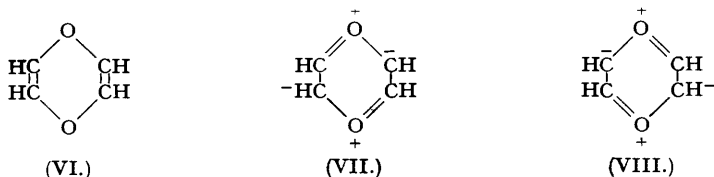
(ii) *Consideration of only adjacent formal charges.* In discussing the small resonance energy of the vinyl ethers, relative to furan, Wheland (*op. cit.*) pointed out that the formal charges are separated in the ionic structures (I) ascribed to the former, but can be on adjacent atoms for the



furan structure as in (II). He suggested, in consequence, that the main contribution to the stabilisation of the furan molecule is due to structures such as (II) and that those such as (III), in which the formal charges are separated, play only a small part. A relatively high electron density in the 2-position is, moreover, in accord with the orientation effects observed in substitution reactions. This view can be placed on a quantitative bases. Furan, for example, can be represented by the 3-orbital-4-electron systems shown in (IV) and (V). The resonance energy of the corresponding hydrocarbon analogue—the allyl anion—is 0.83β , in fair agreement



with the empirical values for furan. In the same manner, 2-vinylfuran would be represented by a 5-orbital-6-electron system for which an additional resonance energy, above that for the furan molecule, of 0.64β was derived. This is, however, about twice the empirical energy 0.3β , and is in poorer agreement than the simple molecular-orbital treatment which, somewhat surprisingly, gives the low value, 0.44β . Furthermore, the dioxadien molecule (VI) would presumably be accorded an unacceptably large resonance energy on Wheland's view, as two pairs of adjacent charges are present in the ionic structures (VII) and (VIII) (Summerbell and Umhoefer, *J. Amer. Chem. Soc.*, 1939, 61, 3020).



In general it is felt that Wheland's suggestion, while often of value in a qualitative way, is unlikely to form a useful basis for quantitative treatment. Modified parameters could be introduced in the calculations to allow for the electron affinity of the oxygen atom, but such refinements hardly seem justified.

(iii) *Modifications to the parameters of the secular equation.* As mentioned above, an allowance for the disturbing effect of an oxygen atom can be made by modifying the parameters involved in the simple molecular-orbital treatment (Wheland and Pauling, *loc. cit.*). Such modifications can comprise an adjustment of the Coulomb terms of the oxygen and the adjacent carbon atoms and of the resonance integral for the C-O bonds relative to the C-C bonds. In particular, Wheland and Pauling have made adjustments to the first two parameters in their quantum-mechanical treatment of orientation in the furan nucleus. We now consider the effects of such adjustments on the derived resonance energy of a number of oxygen-containing compounds.

Results obtained by using Modified Parameters.—Furan was taken as the test material in order to assess the dependence of the resonance energy on the magnitude of the Coulombic term assigned to the oxygen atom. The results, given in Table I, show that a change from the normal value W to $(W + 2\beta)$ almost halves the derived resonance energy, while a further modification to $(W + 4\beta)$ produces a relatively small change. The use of the latter term, moreover, yields a resonance energy of 1.1β , close to the empirical value as Wheland and Pauling implied in their paper.

TABLE I.

Calculated values for the resonance energy of furan.

Coulombic terms for the oxygen atom.	Energy (β).		Resonance energy (β).
	Resonating molecule.	Non-resonating molecule.	
W	6.48	4	2.48
$W + 2\beta$	9.37	8	1.37
$W + 4\beta$	13.1	12	1.1

As a consequence, the term $(W + 4\beta)$ was retained and an examination made of the effect of varying the Coulombic term for the carbon atoms in positions 2 and 5. The results obtained show the calculated resonance energy to be insensitive to variations in the range W to $(W + 0.5\beta)$ (Fig. 1). Consequently, while these Coulombic terms require adjustment to account for substitution in the furan nucleus, they may be neglected so far as the derivation of

resonance energies is concerned. Naturally, such an adjustment becomes more significant in resonating systems smaller than furan—as, for example, vinyl ether (Table II)—but the decrease which accompanies its use will tend to be offset by the increase which would obtain if a larger resonance integral for the C—O bond were used. Such a modified resonance integral is formally required, as the difference between the strengths of the C=O and C—O bond is about twice that for the C=C and C—C bond. On the whole, therefore, it seemed reasonable to consider only an adjustment to the Coulombic term of the oxygen atom, particularly as this leaves the calculations relatively simple. To test this view, calculations were carried through for a number of oxygen-containing compounds of known resonance energies. The results are given in Table II which includes, for comparison, the values given by the unmodified molecular-orbital method. The latter are, as expected, uniformly too large, most noticeably so with divinyl ether which has the low empirical resonance energy of 0.2β .

TABLE II.
Resonance energies of vinylfuran, phenol, and the vinyl ethers.

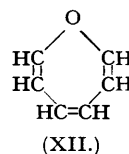
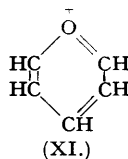
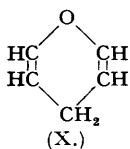
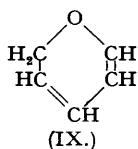
	Coulombic term for the oxygen atom.	Energy (β).		Resonance energy (β).	
		Resonating molecule.	Non-resonating molecule.	Calc.	Empirical.
Vinylfuran	W	8.92	8.48	0.44	—
	$W + 4\beta$	15.57	15.1	0.47	0.3 ³
Ethyl vinyl ether	W	2.83	2	0.83	—
	$W + 4\beta$	10.20	10	0.20	—
	$W + 4\beta$	10.34	10.56	-0.22 ¹	—
	$W + 4\beta$	11.29	10.56	0.73 ²	0.2
Phenol	W	8.72	8	0.72	—
	$W + 4\beta$	16.19	16	0.19	0.45 ³
Divinyl ether	W	5.46	4	1.46	—
	$W + 4\beta$	12.48	12	0.48	0.2

¹ "Strain" energy, calculated by using $(W + \frac{1}{2}\beta)$ on the carbon atoms adjacent to oxygen.

² Calculated as above, but by use, in addition, of 2β for the C—O resonance integral. ³ Additional resonance energy.

The modified values are generally much lower, as is required, and are in fair agreement with the empirical figures. The least satisfactory is divinyl ether where the calculated resonance energy is twice the small empirical value. A change in the Coulombic term, from W to $(W + \frac{1}{2}\beta)$, on the carbon atoms adjacent to oxygen would reduce the calculated resonance energy as required, but the use of such an adjustment would then result in poorer agreement for the other compounds. With ethyl vinyl ether, for example, a "strain" and not a resonance energy would be derived by its use (see Table II). In consequence it was decided to work only with the modified Coulombic term $(W + 4\beta)$ for the oxygen atom in the subsequent calculations.

Consideration of Various Heterocyclic Compounds—Among the heterocyclic compounds to be considered are those containing oxygen, with structure (IX)–(XII). The unmodified molecular-



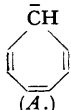


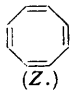
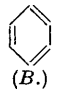
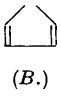
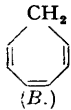


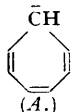
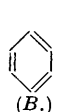
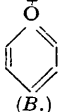
orbital treatment ascribes a resonance energy of 1.46β to 2-pyran (IX), a value larger than the empirical value for furan. Such a value seems quite inconsistent with the failure of attempts to prepare the substance. A much lower and more satisfactory value, 0.68β , is given by the modified treatment. 4-Pyran (X) is accorded the same high stability as 2-pyran on the unmodified treatment, but an even lower resonance of 0.48β by the corrected method. The cyclohexadiene structure (VI), previously considered, may now be re-examined. It should have the same high stability as benzene, according to the unmodified method, but a figure of 0.75β , in much better agreement with its behaviour, is given by the corrected method (Beach, *J. Chem. Physics*, 1941, 9, 541).

The disturbing effect produced by oxygen in lowering the resonance energy of a conjugated system will become less pronounced as the size of the system increases. As an interesting example, the pyrylium cation (XI) was treated by both methods. The calculated resonance energy decreased only from 2β to 1.74β . Naturally, apart from this high degree of internal

stability, a full treatment of such an ionic structure would involve consideration of its lattice and solvation energies.

A further example of the larger conjugated system is the seven-membered cyclic triene (XII). Its hydrocarbon analogue is the *cycloheptatrienyl* anion whose resonance energy, by molecular-orbital calculations, is 2.1β (Hückel, The Physical Society, "Internat. Conf. on Physics," 1935, 2, 9). The modified method of calculation applied to (XII) will reduce this value, but to an extent smaller than that previously noted for the corresponding pair, *cyclopentadienyl* anion and furan, where the change is from 2.48β to 1.1β (Table I). In consequence, (XII) is likely to have a resonance energy about 1β . In agreement with this, calculation gives the value $(15.28 - 14.0)\beta = 1.28\beta$, which is higher than that for furan. In addition to the *cycloheptatrienyl* structure, a number of other structures may be used as a basis for estimating the resonance energy of (XII). Such comparative methods may be useful when the empirical or calculated value is unknown. The details of these methods are summarised in Table III, which also indicates where calculated or empirical values are used and whether the top molecular orbital is bonding or anti-bonding in type.

TABLE III.
Resonance energy of the cyclic triene (XII) by comparative methods.

Com- parison no.	Replac- ement procedure.	Modification corresponding to (XII)		Related change.		Deduced resonance energy of (XII) (β).
		Structure.†	Resonance * energy (β).	Structures.†	Resonance * energy change (β).	
1	-O- by $\bar{\text{C}}\text{H}$	 (A.)	2.1 (m.o.)	 to  (B.) (B.)	2.48 (m.o.) to 1.1 (e)	~ 1
2	-O- by -CH=CH-	 (Z.)	1.68 (m.o.)	 to  (B.) (B.)	2 (e) to 1.1 (e)	~ 1
3	-O- by -CH ₂ -	 (B.)	0.3 (e)	 to  (B.) (B.)	0.16 (e) to 1.1 (e)	~ 2
4	—	 (A.)	2.1 (m.o.)	 to  (B.) (B.)	2.0 (e) to 1.74 (e)	~ 2

* (m.o.) indicates a calculated and (e) an empirical resonance energy.

† (A) represents a top molecular orbital which is anti-bonding, (B) one that is bonding, and (Z) one that is neither bonding nor anti-bonding.

When *cyclooctatetraene* is taken for comparison 2 (Table III), the resonance energy (1.68β) calculated for the planar molecule is used rather than the small empirical energy (0.3β) for the actual buckled molecule (Prosen, Johnson, and Rossini, *J. Amer. Chem. Soc.*, 1949, 69, 2068).

It will be observed that the comparisons given in Table III place the resonance energy of (XII) in the range 1— 2β . The reliability of the individual methods is not, however, the same. It will be less where the comparison of one structure having only bonding molecular orbitals is made with others which have non-bonding or anti-bonding molecular orbitals. This criticism applies to methods (1), (2), and (4). Method (3) is unsatisfactory because it involves a comparison of an open-chain resonating group with a cyclic group. Moreover, in (1) and (4) both charged and neutral molecules are involved in the comparison. In spite of these criticisms, it is evident that the comparative method gives a fair indication of the resonance energy in this instance.

In some instances, heterocyclic nitrogen compounds may also be considered on the present basis. As the electron affinity of nitrogen—though less than that of oxygen—is greater than

that of carbon, the replacement of a CH group by a nitrogen atom should reduce the resonance energy * (cf. Dewar, *Trans. Faraday Soc.*, 1946, **42**, 754). This particular replacement is, moreover, normally taken as leaving the resonance integral unchanged (Coulson and Longuet-Higgins, *Trans. Faraday Soc.*, 1947, **83**, 43; Coates and Sutton, *J.*, 1948, 1187). Thus it is customary to use only a modified Coulombic term ($W + 2\beta$), for the nitrogen atom, which indeed gives a suitable value for the resonance energy of pyrrole, at about 1.5β (cf. Table I). As an

FIG. 1.

The effect on the derived resonance energy of modifying the Coulomb term for carbon atoms 2- and 5- in furan.

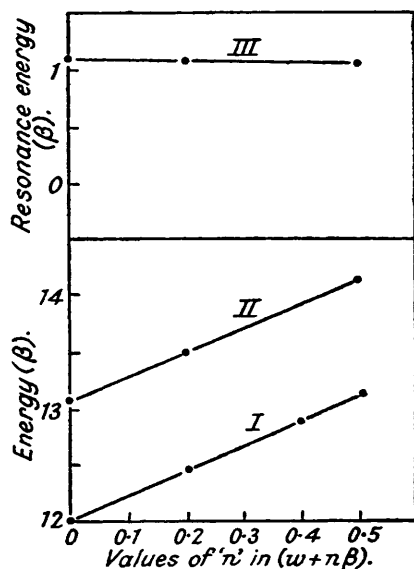
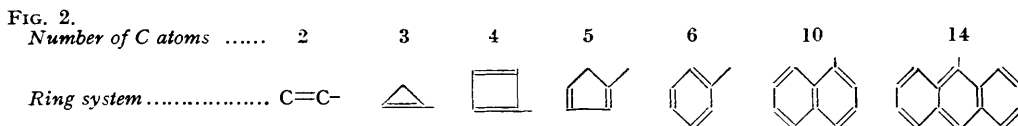
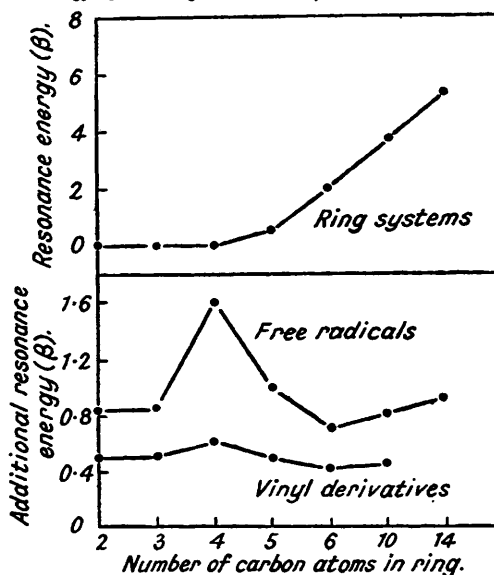


FIG. 1. I, Energy of lowest non-resonating structure. II, Ground-state energy. III, Resonance energy.

FIG. 2.

Comparison of additional resonance energy of vinyl derivatives and free methylene radicals with the resonance energy of the ring to which they are attached.



example, the substitution of nitrogen for the relevant CH group in (IX) gives 1 : 4-oxazine which like the parent, 2-pyran, is also unknown. In view of its low resonance energy, we would not therefore expect 1 : 4-oxazine to be formed by the dehydrogenation of morpholine, its tetrahydro-derivative.

Finally, calculations were made for the furfuryl radical and radical ions (see Table IV). In particular, they show the resonance energies of the free radical and the cation to be little affected by the use of the modified Coulombic term on the oxygen atom. It is unfortunate that no experimental values are available for comparison.

Discussion.—While the resonance energy of furan is less than that calculated by the simple molecular-orbital method, the results given in Tables II and IV show the additional resonance energy of vinylfuran and of the furfuryl radical to be almost the same whether the simple or the modified molecular-orbital treatment is used. While such a result may be dependent on the basic assumptions of the methods used, it implies, if real, the additional resonance energy ascribed to an appendage to be almost independent of the resonance energy of the group to which the appendage is attached. Such a conclusion is, in fact, borne out by calculation in the hydrocarbon field. Thus the additional resonance energies, given by the molecular-orbital method, for both

* Empirical values for some 6-ring nitrogen compounds, e.g., pyridine, are not apparently consistent with this statement. This may be due to the over-estimation of resonance energies in five-membered rings by the molecular orbital method (Syrkin and Diatkina, *Acta Physicochim. U.R.S.S.*, 1946, **21**, 641).

TABLE IV.

The resonance energies of the furfuryl radical anion and cation.

Derivative.	Coulombic term for the oxygen atom.	Energy (β).		Resonance energy (β).
		Resonating molecule.	Non-resonating molecule.	
Free radical	W	7.21	6.48	0.73
	$W + 4\beta$	13.97	13.10	0.87
Anion	W	6.96	6.48	0.48
	$W + 4\beta$	13.90	13.10	0.80
Cation	W	7.46	6.48	0.98
	$W + 4\beta$	14.04	13.10	0.94

the vinyl and the methylene group attached to ring systems varying from ethylene (a two-membered "ring") through *cyclopropene* and *cyclobutadiene* to naphthalene and anthracene are shown in Fig. 2. But for a curious jump for the (unknown) *cyclobutadiene* derivatives, the additional resonance energy of the vinyl derivatives is around 0.4β (cf. Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, 195, 188), whereas the value for the substituted methyl derivatives is about twice as great (around 0.8β), and this, even when the resonance energy of the ring systems varies from 0β to 5β . The same conclusion can be drawn from molecular-orbital calculations for conjugated olefin structures, where the corresponding additional resonance energies tend to 0.54β and 1.27β , respectively, as the chain length increases (Hückel, *loc. cit.*). While these values seem qualitatively correct for vinyl compounds, in view of their ready polymerisation, they are somewhat larger than the empirical resonance energies, where comparison is possible. By contrast, the calculations give too low a value for the resonance energy of the free benzyl radical (cf. Szwarc, *Faraday Soc. Discussion*, 1947, **2**, 39). However, the approximate constancy of the resonance energies derived in these calculations seems to agree with experiment, as indicated by the results for the allyl, 2-methylallyl, benzyl, and picolyl free radicals (Szwarc *et al.*, *J. Chem. Physics*, 1948, **16**, 128, 981; 1949, **17**, 284, 292; Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339). As the calculated values for vinylfuran and the furfuryl radical are similar to those derived for the corresponding hydrocarbons, it appears, somewhat surprisingly, that little change in self-polarizability can result from the presence of the ring oxygen atom (Coulson and Longuet-Higgins, *loc. cit.*).

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