571. *Conjugation in Unsaturated Systems Containing Hetero-atoms. Part II.*[1] *Refined Treatment of Isoxazole, the Phenylisoxazoles, and the Benzisoxazoles*

By Gaston Berthier and Giuseppe Del Re

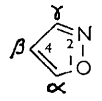
A refined semi-empirical study of the π-systems of isoxazole, phenylisoxazole, and benzisoxazole has been carried out. The purpose of this study was (a) to see how the results previously obtained by the Hückel method were affected by the inclusion of antisymmetrisation and long-range effects, and (b) to ascertain to what extent the criteria and definitions used in Part I for interpreting the results could be considered to be valid in more complicated treatments. As concerns (a), the new results are encouraging, for they just show a slight improvement of the good agreement with experimental data already found with the Hückel method. The refined treatment sheds more light on the importance of mutual polarisation in the conjugation of different units.

As concerns (b), the use of the refined method has led to a revision of the concept and definition of interaction energy, introduced in Part I to measure the interaction of two π-systems. One can define an "extra-delocalisation energy" and a "π dissociation energy"; the values of the latter quantity are in agreement with the expected order of stability of the combined isoxazole–benzene systems; those of the former appear to be more strictly related to polarisation effects. Together with the other results, this suggests that definitions and criteria valid beyond the limits of the numerical results can be obtained, but a test of them by a refined scheme is essential to ensure that special simplifying features of the original method do not lead to ambiguities.

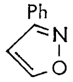
It is concluded that a semi-empirical treatment of the Hückel type can be both a sufficient tool for the chemist and, under the above conditions, a scheme within which quite sound and lasting analyses of fact can be performed.

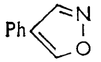
In Part I,[1] one of us applied the Hückel method to the π-electrons of the phenylisoxazoles. That study was intended not only to reach a better understanding of the compounds studied, but to define and test the quantities to be used for the interpretation of chemical facts within the frame of a π-electron theory. It also served as a further test of the method and parameters already used for isoxazole [2] and the benzisoxazoles.[3]

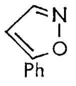
In the present Paper we shall discuss the results obtained for the same compounds (Figure 1) when, still within a semi-empirical scheme based on a strong σ–π separation, one introduces antisymmetrisation and carries the treatment to self-consistency. Such a discussion should help to assess more readily the general validity of concepts introduced within the oversimplified scheme of the Hückel method, and to see to what extent the removal of some of the simplifying features inherent in the latter method would modify the conclusions to which it led us in connection with the compounds mentioned above.

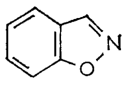


isoxazole

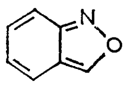








indoxazene



anthranil

Method.—The calculations were carried out according to a scheme elaborated by one

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[1] Part I, G. Del Re, *J.*, 1962, 3324.

[2] L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113.

[3] G. Del Re, *Tetrahedron*, 1960, **10**, 81.

of us.[4] An IBM 7090 computer was used, the complete calculations taking an average of 30 sec. per molecule.

Some features of the method are worth explicit mention here.

The calculations concern only the π-electrons of the compounds under consideration, the σ core being considered as frozen. They refer to a basis χ of strictly atomic orbitals, but were carried out *via* a basis λ of orthogonalised atomic orbitals, related to χ and to the corresponding overlap matrix S by the equation:[5]

$$\lambda = S^{-\frac{1}{2}}\chi \qquad (1)$$

The use of the orthogonalised orbitals as an intermediate basis was suggested by technical considerations, consisting partly of the fact that, when it is employed, certain aspects of the Pariser–Parr formalism (like the zero-differential overlap approximation[6,7]) can be formally retained without contradiction of the fully localised nature of the actual atomic orbitals. In fact, to the first order in S, our procedure is equivalent to one using directly the basis χ with the so-called Mulliken approximation for two-electron integrals.[8,9]

The $2p\pi$ Slater orbitals were chosen as the elements of χ. They were assigned the usual effective charges for all calculations but those of the two-electron integrals. In the calculation of the latter, effective charges reproducing the spectroscopic values of the two electron one-centre integrals were used,[10] thus taking approximately into account the correlation effects. The values of the latter effective charges (1·854, 2·080, 2·566 for carbon, nitrogen, and oxygen), as well as those of the one-centre integrals (9·87, 11·07, and 13·66), were the same as those given in a previous Paper,[11] the use of more recent spectroscopic data[12,13] bringing insignificant changes.

The core integrals α_p and β_{pq} were calculated according to the formulæ

$$\alpha_p = W_p - (n_p - 1)(pp/pp) - \sum_{q \neq p} (qq/pp), \qquad (2)$$

$$\beta_{pq} = \tfrac{1}{2}S_{pq}(\alpha_p + \alpha_q) - kS_{pq}. \qquad (3)$$

Here the symbol (pp/qq) represents the two-electron Coulomb integral involving the $2p\pi$ orbitals of the atoms p and q; W_p is the ionisation energy of *one* electron of p in its valence state ($W_N = W_C - 2{\cdot}46$ ev; $W_O = W_C - 3{\cdot}21$ ev); n_p is the number of electrons shared by p with the π system under study; S_{pq} is the overlap integral between p and q; k, the only quantity estimated from molecular data (namely, the spectrum of benzene[14]), is assumed to be a constant independent of the nature and length of the $p - q$ bond (8·525 ev).

The above choice of k is largely arbitrary. This is due to the fact that no criterion for estimating it on a sounder basis has as yet been found. Nevertheless, the very simplicity of the assumption that k is a constant compensates, in our opinion, for its obvious approximate nature, especially in view of the fact that we consider here compounds where the hetero-atom system is always the same, and the changes in the substituents affect very little the heterocyclic component. We add that the dipole moment and the various energies (including transition energies) for isoxazole itself do not vary to any important extent if the constant k is changed for a particular bond. For instance, a 10% change in its value for the N–O bond of isoxazole gives only a 3% change in the dipole moment and a 1% change in the transition energy.

[4] G. Berthier, J. Baudet, and M. Suard, *Tetrahedron*, 1963, **19**, Suppl. 2, 1.

[5] P. O. Lowdin, *J. Chem. Phys.*, 1950, **18**, 365.

[6] R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

[7] J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[8] K. Ruedenberg, *J. Chem. Phys.*, 1951, **19**, 1433.

[9] G. Del Re and R. G. Parr, *Rev. Mod. Phys.*, 1963, **35**, 604.

[10] A. Julg, *J. Chim. Phys.*, 1958, **55**, 413; 1959, **56**, 235.

[11] M. Suard, G. Berthier, and B. Pullman, *Biochim. Biophys. Acta*, 1961, **62**, 254.

[12] G. Pilcher and H. A. Skinner, *J. Inorg. Nuclear Chem.*, 1962, **24**, 937.

[13] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

[14] J. Baudet and G. Berthier, *J. Chim. phys.*, 1963, **60**, 1159.

The coefficients c_{pi} of the molecular orbitals

$$\phi_{\text{i}} = \sum_{\text{p}} c_{\text{pi}}\lambda_{\text{p}} \qquad (4)$$

were determined *via* the density matrix R, the general element of which is

$$R_{\text{pq}} = \sum c_{\text{pi}}c_{\text{qi}} \qquad (5)$$

according to the method of the modified density matrix.[4] This method consists essentially in varying R according to the formula:

$$\delta\text{R} = g[(1 - \text{R})\text{hR} + \text{Rh}(1 - \text{R})] \qquad (6)$$

where g is so chosen that R will commute with the Hamiltonian h which defines it. Upon reaching the self-consistency of R, the c's of equation (4) were determined by finding the eigenvectors of h.

Geometrical Data.—The isoxazole molecule was assumed to be planar, the distances being given in Table 1.

TABLE 1

Interatomic distances in isoxazole

Pair of atoms	ON	OC_3	OC_4	OC_5	NC_3	C_3C_4	C_4C_5
Distance (Å)	1·32	2·14	2·16	1·37	1·25	1·44	1·34

The benzene rings of the phenyl- and benz-isoxazoles were assumed to be coplanar with isoxazole, the axes of the phenyl groups of the former coinciding with the bisectrix of the angle of isoxazole to the vertex of which they were linked. The C–C distance in benzene was assumed to be 1·40 Å; the C(phenyl)–C(isox.) distance was taken as equal to 1·44 Å. The lengths of the isoxazole bonds common with the benzene ring in the two benzisoxazoles were taken as equal to the aromatic bond length.

The above geometrical data differ from those used for calculating dipole moments in the Hückel calculations,[1,3] where the isoxazole and the benzene rings were supposed to be regular polygons with sides 1·39 Å long.

RESULTS AND DISCUSSION

General Remarks.—As in Part I, we consider the energies, the charges, the dipole moments, and the u.v. spectra of the isoxazoles of Figure 1.

The essential features of the interpretation of experimental facts derived in Part I and ref. 3 appear to be valid also with the refined treatment, which only adds a few quantitative improvements. As could be expected, difficulties in the comparison of the two treatments, especially as concern energies, arise from the fact that the present method takes more detailed account of the molecular structure and of the different kinds of interactions between atoms.

Energies.—In Part I we defined the interaction energy of the π-systems of two conjugated units A and B as the difference between the total calculated energy of the combined AB π-system and the sum of the energies calculated for the π-electrons of the isolated units; in the Hückel method the latter was obtained by suppressing the binding between the two units, *i.e.*, by setting the corresponding bond integral equal to zero.

The quantity thus defined could be considered both as a measure of the additional stabilisation accompanying the change in delocalisation brought about by the establishment of a link between the two units and as a measure of the global binding effects due to the interaction of the two π-systems. In the more complete scheme used here one cannot find a single quantity susceptible of both interpretations. This is related mainly to the explicit inclusion of the two-electron terms in the energy expression, and of non-vanishing core parameters for atoms of the two units which are not linked in the chemical formula.

Therefore, if we still want to discuss the interaction of two π-systems through a connecting link in terms of energy differences, we have to consider two different cases:

(*a*) A measure of the delocalisation effects can be obtained, following Mulliken,[15] by calculating the difference ΔE_{del} between the actual calculated energy of the AB π-system and the energy the same system would have if the electron distributions in the individual units A and B were not affected by their juxtaposition, *i.e.*, if it were described by an antisymmetrised function reducing to the product of the Slater determinants describing within the same theoretical scheme the individual units.

The procedure used for the calculation of ΔE_{del} (which we may call " extra delocalisation energy ") is worth describing. The results of our calculations are given in terms of the orthogonalised basis λ, the elements of which depend on all the atoms of the system under study. Now, let $C^{\lambda}{}_{A}$ and $C^{\chi}{}_{A}$ denote the matrices of the coefficients of the molecular orbitals of A in the two bases; then

$$C^{\chi}{}_{A} = S^{-\frac{1}{2}}{}_{A}C^{\lambda}{}_{A} \tag{6}$$

S_A being the overlap matrix of A. The matrix of the coefficients representing the two non-interacting units A and B will then be:

$$C^{\chi}{}_{A,\mathbf{B}} = \begin{vmatrix} C^{\chi}{}_{A} & O \\ O & C^{\chi}{}_{\mathbf{B}} \end{vmatrix}, \tag{7}$$

so that

$$C^{\lambda}{}_{A,\mathbf{B}} = S^{-\frac{1}{2}}\, C^{\chi}{}_{A,B}, \tag{8}$$

S being the overlap matrix of the AB π-system. We now make the transformation:

$$\tilde{C}^{\lambda}{}_{A,\mathbf{B}} = C^{\lambda}{}_{A,\mathbf{B}}(C^{\lambda}{}_{A,\mathbf{B}}\, C^{\lambda\dagger}{}_{A,\mathbf{B}})^{-\frac{1}{2}}, \tag{9}$$

and calculate the energy for the two unperturbed systems by the usual formula for Slater determinants. The last step is necessary in order to make the left-hand member of equation (8) unitary, but does not change the energy value.

The physical reason for the above procedure is that, whenever electrons are to be localised in a certain region of a molecule, the localisation has to be referred to the primitive non-orthogonal basis of atomic orbitals. We also emphasise that in the above calculation the geometrical arrangement of the two units is supposed to be the same as in the actual AB molecule, so that ΔE_{del} corresponds to the actual calculated energy minus the energies of the isolated units, the energies of interaction of the core of A with the unperturbed π-system of B and *vice versa*, and the Coulomb interaction energies between the unperturbed π-electron clouds of A and B, including the exchange terms arising from antisymmetrisation.

Table 2 gives the calculated values of ΔE_{del} for the phenylisoxazoles. The results of the Hückel calculations are confirmed for the 5- and 3-derivatives; but the order of the 3- and 4-phenylisoxazole is inverted. This is somewhat surprising in view of the fact that the order obtained by the Hückel method was supported by chemical intuition, the 4-position of isoxazole being its " aromatic " position; and that the experimental evidence, the Hückel calculations, and the present calculations all give transferred charges and interaction dipole moments supporting the 5-3-4 order.

(*b*) A measure of the total contribution of the π-electrons to the binding between the two systems can be obtained by calculating the contribution D_{π} of the π-electrons to the dissociation energy of the ring–ring C–C bond, which we shall call " π-dissociation energy." The dissociation energy of AB into A + B is the difference between the changes ΔE_{el} and ΔR_{nucl} in the electronic and nuclear-repulsion energies when the length of the link connecting A to B goes to infinity.

Let us assume the nuclei to behave as fixed attraction centres for each geometrical

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[15] R. S. Mulliken and R. S. Parr, *J. Chem. Phys.*, 1951, **19**, 1271.

configuration (Born-Oppenheimer approximation); then the change in nuclear repulsion would be $\sum_{ij} Z_i^A Z_j^B / r_{ij}$ (i and j being atoms belonging to A and B, respectively, situated at a distance r_{ij} and having nuclear charges Z) if the σ, π, and inner core electrons were all taken into account in the electronic problem. In our case, where we consider only the π-electrons, the electron-nucleus attraction terms are not terms of the type $Z_i/r_{i\mu}$, i denoting a nucleus and μ an electron, but terms of the type [6]

$$I_{pp} = W_p - \sum_{q \neq p} n_q(pp/qq) - \sum_{Q \neq p} (Q : pp), \tag{10}$$

and therefore the Z's appearing in the expression for the nuclear repulsion should be given a complicated expression. Now, consistently with equation (10), and with our neglect of penetration integrals [denoted by $(Q : pp)$], we can use an argument strictly parallel to that developed by Parr and Pariser,[16] but taking into account the fact that a hetero-atom may contribute more than one electron to the π-system. We thus find

$$\Delta R_{nucl} = \sum_{p \text{ in A}, } \sum_{q \text{ in B}} n_p n_q (pp/qq) \tag{11}$$

The other quantity ΔE_{el} is obviously the total electronic energy E_{el} of the AB π-system minus the sum of the electronic energies of A and B separately. If A and B are identified with the benzene and isoxazole π-systems, we can write

$$\Delta E_{del} = E_{el} - (E_{benz} + E_{isox}); \tag{12}$$

the π dissociation energy D_π of a phenylisoxazole is thus

$$D_\pi = -(\Delta E_{el} + \Delta R_{nucl}), \tag{13}$$

where the right hand member is defined in equations (11) and (12).

The fifth column of Table 2 gives the values calculated for D_π according to the above procedure. All the values are very small, and the order is the more reasonable order 5–3–4, the value for 4-phenylisoxazole being negative, *i.e.*, corresponding to a repulsion of the two π-electron systems.

TABLE 2

Total and interaction energies in the phenylisoxazoles

	$-E_{el}$	$-E_{el}'$	ΔR_{nucl}	$-\Delta E_{del}$	D_π
3-Phenylisoxazole	483·9514	483·6955	125·3161	0·2559	0·0130
4- ,, ...	482·4989	482·2161	123·9404	0·2828	−0·0638
5- ,, ...	493·9174	493·6078	135·2406	0·3076	0·0545

* All energies in ev. The symbols have the following meanings: E_{el} is the total calculated electronic energy; E_{el}' is the electronic energy calculated without change in delocalisation with respect to the isolated benzene and isoxazole π-systems; ΔR_{nucl} is the nuclear repulsion term corresponding to the π-electrons [see equation (11) of the text]; $\Delta E_{del} = E_{el} - E_{el}'$ is the extra delocalisation energy; $D_\pi = -(E_{el} + E_0 + \Delta R_{nucl})$ is the π dissociation energy of the bond linking benzene to isoxazole [equations (12) and (14)], where $E_0 = -(E_{benz} + E_{isox}) = 358{\cdot}6223$ ev.

In view of the preceding arguments and of the Discussion of Part I, Table 2 suggests that the quantity D_π is preferable to ΔE_{del} as an overall measure of the interaction of two π-systems. However, if D_π has a more direct physical significance, it is not the measure of a special conjugation effect; therefore, in so far as the practice of analysing physical situations in terms of perturbing effects on a reference state is acceptable, a knowledge of ΔE_{del} is valuable, as it represents the energy contribution due to the delocalisation effect accompanying the linking of two units.

We also note that, whereas the definition of D_π is not artificial but for the σ–π separation it involves, the actual calculated values may not correspond quantitatively to the entire contribution of the π-electrons to the dissociation energy for the bond between the rings; in fact, in addition to the semi-empirical features of the method used, we must remember

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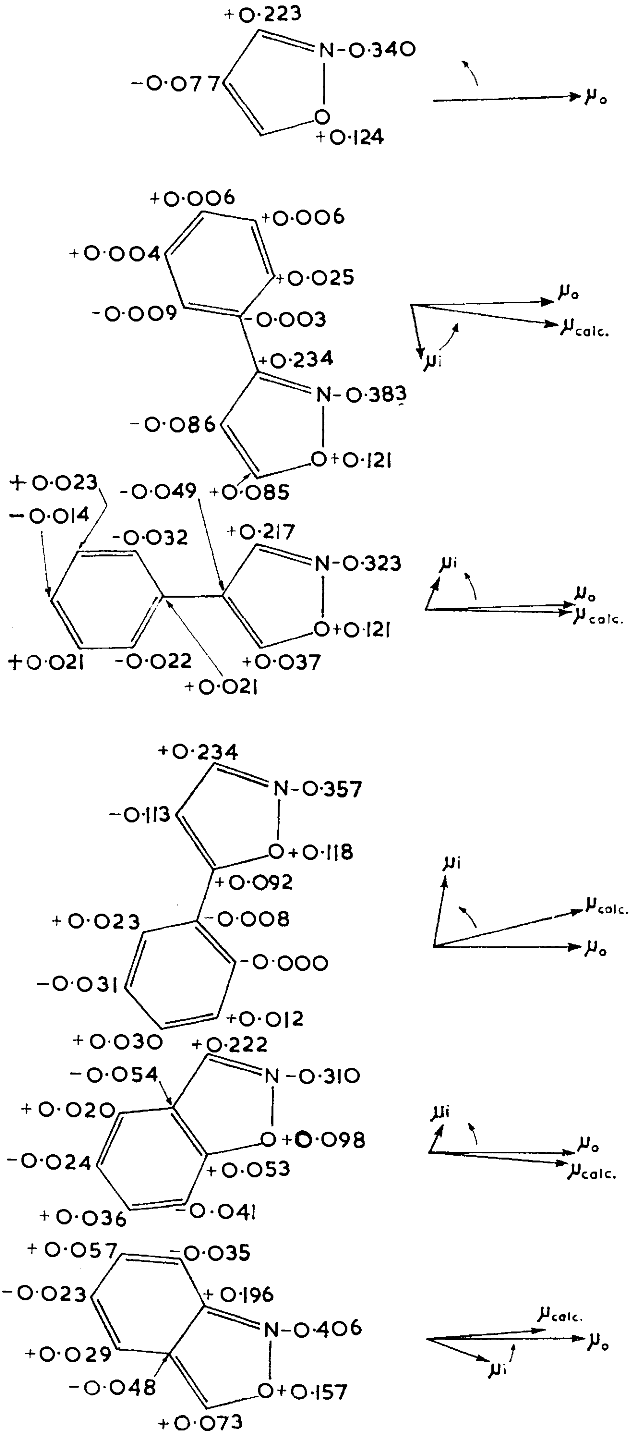
[16] R. G. Parr and R. Pariser, *J. Chem. Phys.*, 1955, **23**, 711.


+0·223
N-0·340
-0·077
O
+0·124
μ_o
+0·006
+0·006
+0·004
+0·025
-0·009
-0·003
μ_o
$\mu_{calc.}$
μ_i
+0·234
N-0·383
-0·086
O+0·121
+0·023
-0·014
-0·049
+0·085
-0·032
+0·217
N-0·323
O+0·121
μ_i
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-0·022
+0·037
+0·021
+0·234
N-0·357
-0·113
O+0·118
+0·092
μ_i
$\mu_{calc.}$
μ_o
+0·023
-0·008
-0·000
-0·031
+0·012
+0·030
+0·222
-0·054
N-0·310
+0·020
O+0·098
μ_i
μ_o
$\mu_{calc.}$
-0·024
+0·053
+0·036
-0·041
+0·057
-0·035
-0·023
+0·196
N-0·406
$\mu_{calc.}$
μ_o
+0·029
μ_i
-0·048
O+0·157
+0·073

FIGURE 2

that no allowance has been made for the so-called σ-core polarisation. Therefore, the values of Table 2 must be used as a means of analysis of the results of the calculations rather than as a set of values to be compared with experiment. In this sense, they are significant even though they are very small. Finally, we note that the very fact that both the ΔE_{del} and D'_π values are very small indicates that such effects as the above mentioned σ-core polarisation are negligible in the phenylisoxazoles.

Charges and Dipole Moments.—These quantities have been derived from the diagonal elements of the density matrix for the basis λ (net charge of p: $\mathrm{q_p} = \mathrm{n_p} - 2\mathrm{R}^{\lambda}{}_{\mathrm{pp}}$; dipole moment: $\mu_\pi = \sum_{\mathrm{p}} \mathrm{q_p r_p}$, $\mathrm{r_p}$ being the position vector of p); they are given in Table 3, and Figure 2. In accordance with a previously obtained result,[17] the charges thus defined are such that their dipole moment, calculated by the above formula as if they were centred on the various nuclei, coincides with that obtained by the usual formulæ including explicitly overlap moments, but for a negligible correction.

TABLE 3

Transferred and root mean square charges on the phenyl groups of the phenylisoxazoles

Substituted position	3	4	5
Transferred charge (Hückel *)	0·043	−0·022	0·041
,, ,, (pres. meth.)	0·029	−0·003	0·025
Root-mean-sq. charge (Hückel) *	0·012	0·006	0·011
,, ,, (pres. meth.)	0·011	0·023	0·021

* The Hückel charges are divided by 1·6 (see text) to make them comparable with those obtained by the present method. The division by 1·6 was performed in refs. 1—3 only for calculating the dipole moments.

The charges found for isoxazole are quite similar to those obtained by the Hückel scheme of Orgel *et al.*,[1-3] divided by 1·6 in accordance with the recipe suggested by those authors to compensate for the use of too large parameters; however, the charges of the 3 and 5 positions are now respectively more and less positive than the Hückel values, in even better agreement with Speroni and Pino's suggestion that position 5 is more positive than position 3.[18]

The charge distributions in the phenylisoxazoles also agree with those given by the Hückel method. The total charges transferred to the phenyl groups (Table 3) compare well, in relative order, with the results of Part I, but the electron-attracting power of the phenyl group linked to the aromatic position 4 of isoxazole appears to be even weaker than was suggested by the Hückel method. However, the perturbation induced by isoxazole on the benzene π-sextet of this compound is not small, in agreement with the values of the extra delocalisation energies of Table 2. In fact, conjugation between two units brings about both a charge transfer and a mutual polarisation. The latter is not negligible for 4-phenylisoxazole; this can be seen without many mathematical elaborations by calculating the root-mean-square charges on the phenyl groups of the phenylisoxazoles (Table 3). Table 3 shows that the agreement between the Hückel and the present calculations is not preserved when a more detailed analysis is carried out. We have here a close parallelism with the discussion of the preceding section. The disagreement between extra delocalisation energies and π dissociation energies found there appears to correspond to the fact that the former depend more strongly than the latter on mutual polarisation effects; and this kind of effect is not taken into due account in the Hückel scheme, at least if the present calculations can be considered as more complete than the Hückel ones.

Also the two benzisoxazoles show agreement in the overall conclusions of the two methods and important disagreements in the details. For instance, the present method suggests that in anthranil it is the enhanced polarity of the N–O bond rather than the higher charge on carbon 5 that determines the peculiar behaviour of this compound; nevertheless,

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[17] G. Del Re, *Nuovo cim.*, 1960, **17**, 644.

[18] G. Speroni and P. Pino, *Gazzetta*, 1950, **80**, 549.

TABLE 4

Dipole moments of isoxazole, phenylisoxazole, and benzisoxazole

	σ moment		π moment		Tot. moment		Interaction moment		Exp †
	μ_σ (D)	θ_σ *	μ_π (D)	θ_π *	μ (D)	θ *	μ_i (D)	α ‡	(D)
Isoxazole	1·93	105°	1·10	56°	2·78	89°	—	—	2·76
3-Phenyl	,,	,,	1·04	83	2·92	98	0·50	80°	2·80
4-Phenyl	,,	,,	1·09	65	2·85	91	0·17	−69	2·95
5-Phenyl	,,	,,	1·67	38	2·99	75	0·71	−79	3·19
Indoxazene	1·78	101	1·09	81	2·83	93	0·22	−71	3·03
Anthranil	1·92	106	1·90	63	3·54	84	0·83	20	3·06

* Θ is the angle with the ON bond of the dipole moment to which it relates (the chemical convention is used). † α is the angle from the isoxazole moment to the interaction moment μ_i. ‡ The experimental values are taken from G. Speroni, " The Chemistry of Heterocyclic Compounds," vol. XVII, chap. V, Wiley, 1962. Where that author gives two values, only his own were accepted, as the other had been obtained from recalculation of less accurate results. The polarisation data also given by Speroni indicate that the experimental error should not exceed ±0·05 D, possible errors due to the fact that the moments were measured in benzene being obviously undetectable.

the qualitative interpretation of its reactions as given in ref. 3 remains unchanged, as it rests on the fact that the C, N pair is more polarised than in isoxazole.

The dipole moments calculated according to the present method are in complete agreement with experiment (Table 4 and Figure 2), even in the case of 4-phenylisoxazole, where a minor disagreement was found with the simpler method. The interaction moments for the phenylisoxazoles (namely, the differences between their total dipole moments and that of isoxazole) show the same picture as that obtained from experimental data and from the Hückel calculations. They are relatively small, although certainly much larger than the relative experimental error; therefore, the agreement with experiment is significant only under the assumption that no relevant polarisation of the σ-core results from the substitution of a hydrogen atom of isoxazole with a phenyl group. This is probably the case in our compounds, whereas, according to a tentative suggestion by Peters,[19] the situation might not be so favourable had we considered different heterocycles.

Excitation Energies and Electronic Spectra.—By the use of the virtual orbitals obtained at the same time as the ground-state occupied orbitals, a number of excited states corresponding to the so-called N–V transitions can be built. In conjugated molecules lacking easily excited lone pairs, the excited states responsible for the first absorption band (singlet) are believed to belong to this type.

The results obtained by our method and by experiment for the compounds of Figure 1 are summarised in Table 5. The qualitative agreement between the two rows of data can be interpreted in terms of bathochromic effects as was done in Part I.

TABLE 5

Spectral data on the isoxazoles

Isoxazole [a]	$\lambda_{\text{max.}}$ = 211 mμ = 5·88 ev	ΔE_{th}* = 4·93 ev
3-Phenyl [a]	= 240 mμ = 5·17 ev	= 4·92 ev
4-Phenyl [a]	= 236 mμ = 5·25 ev	= 4·92 ev
5-Phenyl [a]	= 260 mμ = 4·77 ev	= 4·51 ev
Indoxazene [a, b]	= 280 mμ = 4·43 ev	= 4·83 ev
,, ...	= 245 mμ = 5·06 ev	
Anthranil [c]	= 307 mμ = 4·04 ev	= 3·39 ev
,, ...	= 260 mμ = 4·77 ev	

* ΔE_{th} is the calculated singlet transition energy.

[a] G. Speroni, *loc. cit.* under Table 4. [b] P. Grammaticakis, *Bull. Soc. Chim.* (*France*), 1941, **8**, 101. P. Ramart-Lucas and M. Grumez, *Bull. Soc. Chim.* (*France*), 1950, **17**, 317.

The quantitative agreement between experimental and calculated data is decidedly poor. The approximation consisting in building the excited states starting with the molecular orbitals of the ground state can hardly be the reason for this, as a separate calculation could only lower the energies,[14] and hence further decrease the transition energy. The

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[19] D. Peters, *J.*, 1963, 2015.

disagreement is more likely to be due to the " parameters " used, *i.e.*, essentially to the choice of the proportionality constant *k*. Our value is certainly not the best for the different kinds of bonds appearing in our compounds. However, neither arbitrary changes of *k* nor other empirical corrections designed to improve the agreement in Table 5 would be scientifically meaningful; actually, they would amount to concealing certain defects of the so-called non-empirical methods used nowadays for treating π-systems. Nor would such " refinements " serve any purpose in connection with the present research, where a method more sophisticated than the Hückel method has been applied for better analysing concepts rather than for improving agreement with experiments.

Conclusion.—One question the present research was expected to answer was whether the inclusion of antisymmetrisation and self-consistency in a semi-empirical MO–LCAO π-electron scheme would modify the conclusions reached concerning the chemistry of the compounds under study by the Hückel method. We have seen that there is almost no novelty in that sense, though minor details are changed; this is probably due, at least partly, to the fact that the compounds studied all contain the same heterocycle.

Therefore, the present results give further support to the opinion that the Hückel method with an appropriate choice of parameters is a sufficient tool for the chemist, even in the delicate case of five-membered rings. Actually, the more complete scheme used here is not particularly better, in the sense that it does not seem to solve the well-known problem of obtaining at the same time good ground-state and excited-state wave functions from π-electron calculations. The only difference worth attention between the present results and those of Part I concerns the polarisation effects to which Table 3 refers. These effects appear to be much more marked in the results of the refined method than in those of the simpler one, and are probably related to the fact that the refined method takes into account long-range effects; therefore, one must expect that the Hückel method will not correctly predict mutual polarisation effects, which may take place even when charge transfer and energy effects are very small.

The other question to which the present paper has been devoted is whether the quantities and the criteria used in Part I for analysing and interpreting results could be specified ndependently of the method used for obtaining the numerical results, so as to give that analyses a more lasting value. The preceding discussion confirms once again the impression that this is indeed possible. However, it appears that the definitions in question must be tested in the frame of fairly sophisticated method. In fact, by using only an oversimplified scheme, one is easily led to introduce ill-defined quantities, especially in a π-electron approximation. The most interesting example is the concept of interaction energy, which had been introduced in Part I, and has been resolved here into two different ones; that of extra-delocalisation energy and that of π dissociation energy. The latter has the nature of an observable (and would be an observable, if the σ–π separation had a physical meaning); the former is analogous to the so-called correlation energy, in the sense that, although it cannot be related to any ideal experiment, it measures the weight of certain effects which we usefully consider separately in the binding of two units. Both quantities are now defined without any reference to the method used for obtaining the wave functions.

We conclude that, on one side, the Hückel method may indeed be used as a provisional tool for getting numerical results whenever more rigorous procedures are not practicable; on the other side, the analysis of chemical facts can be carried out by such an oversimplified scheme in such a way that, as more refined methods become available, and the numerical results are replaced by more reliable ones, it may be hoped that the criteria adopted for the analysis remain valid. This requires the use of a very small number of properly defined " theoretical " indices. The employment of more sophisticated semi-empirical schemes is advisable mainly to ensure that the definitions are satisfactory, and, secondarily, to find out if special effects have been neglected in the simpler scheme.

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