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The Electronic Structure of Groups of Isomeric Hetero-Aromatic Systems

I. Derivatives of 1, 2, 4-Oxadiazole

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The electronic structure of the configurational isomers of 3-3′-, 3-5′- and 5-5′-bis-oxadiazole, and of *trans*-α,α'-di-(3-3′)-, -(3-5′)- and -(5-5′)-diazolyl-ethylene, was studied by using the ASMO, SCF, CI procedure developed by Pariser, Parr and Pople. The total π-electron energy is taken as the measure for ranging the various isomers and their different configurations in a given order of stability.

Predictions based on charge distributions and bond orders are in agreement with the chemical behaviour of the known 3-3′ and 5-5′ isomers, and are therefore regarded as reliable also for the 3-5′ compounds, not described in the literature so far.

The calculated value of the lowest singlet transition energy agrees with the observed spectra, with a scatter of ± 0.20 eV depending on the particular procedure chosen for calculating the γ_{pq} and $(A:pp)$ integrals. The calculated second singlet transition is found to depend on the procedure chosen for those integrals to such an extent as to make the prediction unreliable.

La structure électronique des isomères configurationales des 3-3′-, 3-5′- et 5-5′-bis-oxadiazole, et des *trans*-α-α'-di-(3-3′)-, -(3-5′)- et -(5-5′)-diazolyl-ethylène a été étudiée par la méthode ASMO, SCF, CI sélon la forme développée par Pariser, Parr et Pople. L'énergie totale des électrons π a été prise comme étalon pour classifier les isomères et leurs differentes configurations sélon un ordre de stabilité.

Les déductions que l'on peut tirer de la distribution des charges et des ordres de liaison sont en accord avec les observations chimiques des isomères connus, 3-3′ et 5-5′; par conséquent on peut considérer raisonables les prédictions que ont été faites sur les isomères 3-5′, qui ne sont pas décrites dans la literature jusqu'ici.

La valeur calculée pour la première transition de singulet est en bon accord avec le spectre d'absorption observé, l'incertitude due à la procedure choisie pour les integrales γ_{pq} et $(A:pp)$ étant ± 0.20 eV. La deuxième transition de singulet apparait dépendre presque entièrement de la choix faite pour les dites integrales.

Die Elektronenstruktur der Konfigurationsisomere von 3,3′-, 3,5′- und 5,5′-bis-Oxadiazol und *trans*-α,α'-di-3,3′-, -3,5′- und -5,5′-Diazolyläthylen wurde mit Hilfe der ASMO–SCF–CI-Methode studiert. Die totale π-Elektronenenergie wurde als Maß für die Stabilität der verschiedenen Isomere und ihrer Konfigurationen gewählt.

Voraussagen, die auf Ladungsverteilungen und Bindungsordnungen basieren, sind in Übereinstimmung mit dem chemischen Verhalten der bekannten 3,3′- und 5,5′-Isomere und wurden deshalb auch als zuverlässig für die 3,5′-Verbindungen angesehen, die bis jetzt in der Literatur nicht beschrieben sind.

Der berechnete Wert für die niedrigste Singulett-Anregungsenergie stimmt mit den beobachteten Spektren bis auf $\pm$ 0,2 eV überein, abhängig von der Berechnungsart für die γ_{pq} und $(A:pp)$. Die Anregungsenergie für den zweiten Singulettübergang läßt sich in diesem Rahmen nicht vorhersagen.

The theoretical treatment of conjugated hetero-aromatic molecules suffers from several known shortcomings and in general has not reached a measure of quantitative success comparable to that obtained with aromatic hydrocarbons. This situation is partly due to the presence of hetero-atoms, which contribute two π-electrons to the structure, and to the eventual neglect of n-electrons, that necessitate the use of approximations which are much more unsatisfactory than in the case of molecules possessing one π-electron on each atom.

Moreover, the main object of the calculations has been, in most cases, an attempt to account for the lower electronic transitions and relatively few attempts have been made to test the predictive value of the theory towards other properties related to the ground state of the molecules. A step in this direction can be taken, for example, with groups of isomers when they have the same overall π-electronic structure originating from a different arrangement of a few basic units, such as substituents or molecular residues. In these cases there is no systematic means of defining the extent to which reliable predictions can be made about the dependence on the isomeric configuration of certain properties such as total π-energy, electronic transitions, sequence of bond lengths, charge distribution, and of other quantities related to their chemical behaviour.

The recent publication of a series of systematic studies on a group of 1-2-4-oxadiazoles [*3*] offered a chance for an investigation along the lines just mentioned. The molecules we have examined can be divided into two groups, one formed by joining two oxadiazole rings and the other by attaching one oxadiazole ring to each carbon atom of an ethylene molecule, in all the various ways possible. The several configurations which can exist for each group of isomers were examined with the object of answering, as far as possible, the following questions:

a) which configuration of each isomer is predicted as the most stable;

b) what difference should be expected among the lower electronic transitions of the various configurations;

c) how charge distributions and bond lengths are affected by changes in the configuration;

d) to what extent the predictions listed under a), b), and c) depend on the choice of the different approximations used for evaluating the electronic repulsion integrals and on the introduction of the penetration integrals into the core terms of diagonal energy matrix elements.

Our predictions should finally be checked against a set of experimental observations on the known isomers and should stimulate, we hope, further investigations on those compounds which have not been described so far.

The Method of Calculation

The antisymmetrized molecular orbital procedure developed for the π-electron systems by Pariser, Parr, and Pople was followed. We give here the energy matrix element formulae for reference purposes, and add only those details which are related to the choice made among the alternative approximations. The general outline of the theory can be found in standard textbooks [*13*].

Diagonal elements were obtained as

$$F_{pp} = H_{pp}^{\text{core}} + \sum_q P_{pq}\gamma_{pq} - \tfrac{1}{2} P_{pp}\gamma_{pp}$$

with

$$H_{pp}^{\text{core}} = \alpha_{pp}^{\text{core}} = W_p - \sum_{q \neq p} \{(A_q:pp) + n_q\gamma_{pq}\} - \sum_s (A_s:pp)\,,$$

and the off-diagonal as

$$F_{pq} = H_{pq}^{\text{core}} - \tfrac{1}{2} P_{pq}\gamma_{pq}$$

with

$$H_{pq}^{\text{core}} = \beta_{pq}^{\text{core}} = \tfrac{1}{2} S_{pq}(W_p + W_q)\,.$$

Here $(A:pp)$ are the neutral atom penetration integrals with A_q referring to atoms contributing n_q π-electrons to the system, and A_s to the other atoms. S_{pq} are the overlap integrals between $2p\pi$ atomic orbitals of adjacent atoms. When necessary β_{pq} was multiplied by a factor $\cos\vartheta$, ϑ being the dihedral angle between planes of two adjacent rings. The coefficients P_{pq} are defined by

$$P_{pq} = 2\sum_i c_{ip}\,c_{iq}$$

where c_{ij} are the MO coefficients obtained at a given iteration, the sum carried over to occupied MO's. Convergency was obtained up to 10^{-4} in the c_{ij}.

The valence state ionization potentials W_p for core atoms, taken from the data of Hinze and Jaffé [4], are:

$W(C^+) = -11.16$, $W(N^+) = -14.12$, $W(O^{++}) = -34.08$ eV.

The one-center Coulomb repulsion integrals were obtained from the relationship [9]:

$$\gamma_{pp} = 3.29_4\,Z_p$$

by taking $Z(C) = 3.25$, $Z(N) = 3.90$ and $Z(O) = 4.90$.

The two center γ_{pq} integrals were calculated by alternative procedures as follows:

a) For distances where $R < 2.8$ Å, we adopted the formula originally proposed by Pariser and Parr [11]

$$\gamma_{pq} = \tfrac{1}{2}(\gamma_{pp} + \gamma_{qq}) - \lambda R - \mu R^2$$

where λ and μ are determined by parabolic fitting to the values at $R = 2.8$ and $R = 3.7$ Å. For distances where $R > 2.8$, the integral was evaluated by two alternative procedures. In the first we used the Pariser Parr charged sphere formula [11] and refer to it as the PP evaluation. In the second case we used the multipole expansion given by Parr [12] and refer to it as the ME evaluation. This was used in order to deal with integrals where the axes of $2p\pi$ orbitals are no longer parallel because they belong to atoms of different not-coplanar rings*.

b) Using the formula proposed by Nishimoto and Mataga [8]

$$\gamma_{pq} = 14.397/(R + a)\,, \qquad a = 14.397/\tfrac{1}{2}(\gamma_{pp} + \gamma_{qq})\,,$$

referred to as the NM procedure.

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* It should be noted that PP and ME procedures do not give in the planar case significantly different integrals; the changes due to rotation are in most cases of the order of 0.1 eV.

The penetration integrals were calculated by expressing the neutral atom potential operator as a combination of nuclear attraction and electronic repulsion terms [*5*, *15*], and considering the atomic orbitals of the σ-frame as purely trigonal hybrids. Separate calculations were run with and without introducing penetration integrals into the α^{core} terms.

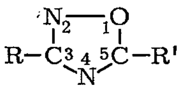
The presence of a methyl substituent on the carbon atoms of the oxadiazole ring was taken into account by introducing the relevant penetration integrals involving the extra-ring carbon.

The ground state SCF π-electron MO's were used as a basis for a configuration interaction treatment which took into account only the four lowest mono-excited configurations.

A tabulation of the basic integrals is given in the appendix.

The Case of Bis-Oxa-Diazoles

The synthesis of unsubstituted and monosubstituted 1,2,4-oxadiazole I was first reported in 1962 [*6*]. So far no X-ray studies have been carried out which could help to define its molecular geometry.



We therefore chose a model based on the average bond lengths found in analogous compounds having atoms bound in the same valence state. The molecular frame we have adopted for the ring is shown in Fig. 1, where the molecular core is also given. The three C–N bonds have been assigned the same length, 1.35 Å, with C–O = 1.32 and N–O = 1.20. Although this model might prove incorrect in various respects* it is not likely that our conclusions will be greatly affected.

The joining of two oxadiazole rings can give rise to three different isomers** according to whether the C–C bond formed is 3-3′, 3-5′ or 5-5′ (the dash indicates the atoms of the second ring). This central bond is assumed to be 1.40 Å long and

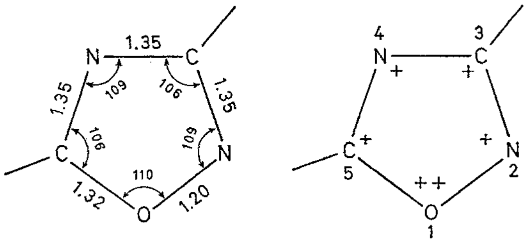


Fig. 1. Molecular geometry and core for 1,2,4-oxadiazole

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* The value of the N–O distance is based on that reported for benzo-furazan (benzo-1,2,5-oxadiazole) [*16*]. More recently a N–O distance of 1.38 Å has been measured [*14*] for 1,2,5-oxadiazole. A calculation for 1,2,4-oxadiazole with this latter value has resulted in a decrease of 0.4 eV in the calculated 1st Singlet → Singlet transition. Charge distribution is much less affected and the same sequence of the C–N bond orders is obtained in both cases.

** Only 3-3′ and 5-5′ compounds have been reported in the Ref. [*3*] so far.

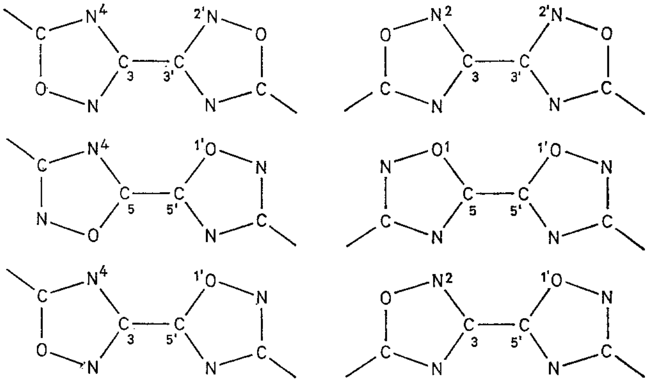

Fig. 2. Different configurations of the planar bis-oxadiazole isomers

to bisect the external angle of the ring. Each isomer can have two different planar configurations. The second one is obtained by rotating the first ring of 180° around the axis of the C–C bond. They are all shown on Fig. 2. We shall identify each one by a notation which designates the isomer by giving the numbers of the joined carbon atoms followed by the numbers, in parenthesis, of the two *cis*, upper, atoms. It can be easily verified that 3-3′(2-2′) and 5-5′(1-1′) belong to the C_{2v} symmetry group, 3-3′(4-2′) and 5-5′(4-1′) to the C_{2h} group, whereas 3-5′(2-1′) and 3-5′(4-1′) are not symmetric. When one ring is rotated with respect to the other through an angle ϑ, the symmetry of both the C_{2v} and C_{2h} systems is lowered to a C_2 group because there remains only a C_2 axis, bisecting the C–C bond and lying on a plane at an angle $\vartheta/2$ with the plane of each ring. It should also be noted that different configurations are obtained from each of the two planar configurations of the 3-5′ isomer by the same rotation of ϑ. These configurations become mirror images when ϑ is 90°.

The question of which of the various isomeric configurations is the most stable is answered by considering the total π-electron energy

$$E_\pi = \sum_i (I_i + \varepsilon_i)$$

where ε_i is the eigenvalue of the ψ_i molecular orbital and $I_i = \langle \psi_i \mid H \mid \psi_i \rangle$, the sommation being carried out over the MO's occupied in the ground state. This quantity represents the energy required to extract all the π-electrons from the molecule, leaving behind the molecular core. It can be used as a good approximation for the comparison of systems whose molecular core is exactly the same as in the present case, and where the change of the total energy of the σ-electrons, resulting from the different geometrical arrangements of the core components, undoubtedly makes a minor contribution*.

In order to compare the various isomers we have therefore taken as zero the lowest (largest negative) E_π calculated by a given approximation and, after subtracting it from the E_π of other isomers, we ranged them all in a succession of increasing differences. The results given in Fig. 3 show that 5-5′(1-1′) is the most

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* For a discussion of these points see the appendix of a previous paper [*1*].

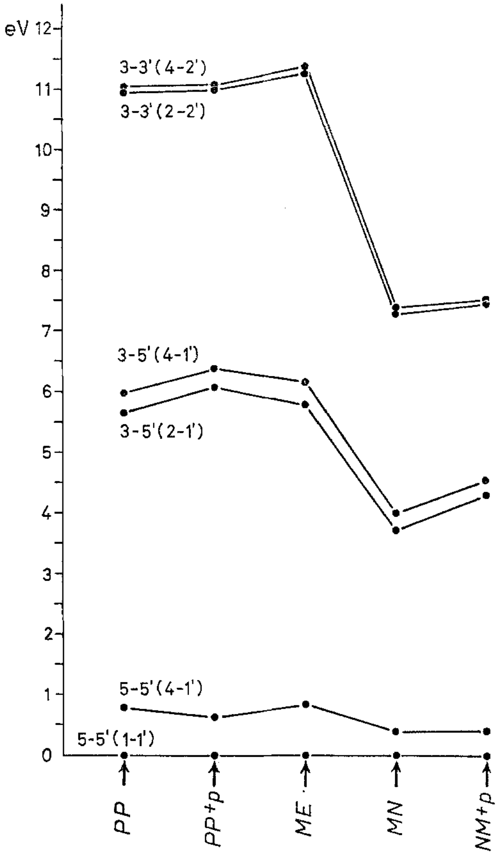

Fig. 3. Comparison of the total π-electron energy of bis-oxadiazole isomers

stable isomer and that the calculated order of stability is independent of the particular approximation used for the γ_{pq} integrals and of the introduction of the penetration integrals. Smaller differences are calculated by the NM than by the PP or ME procedures, but in all cases the relative scaling of the two configurations of each isomer shows a definite trend, being largest with 5-5′ and smallest with 3-3′. This trend has a correspondence in the loss of π-energy which takes place when the two rings are rotated with respect to one another. As shown in Fig. 4, the E_π at 90° of the most stable configuration of each isomer decreases in the same order, the loss being 1.53, 1.17 and 0.90 eV for 5-5′(1-1′), 3-5′(2-1′) and 3-3′(2-2′), respectively. We cannot say that these quantities (calculated with the ME procedure neglecting penetration integrals) are a measure of the rotation energy barrier because our computation completely neglects the energy changes in the σ-frame and in the σ-π interaction which might be of a similar order of magnitude. But we think that a comparison with the measured values would be worth while even if only to ascertain to what extent the neglected terms affect the predicted trend.

The second question asked was about the electronic transitions. The results of our calculations, collected in Fig. 5, show that *within each choice of the procedure* *used for γ_{pq} integrals* (PP and ME being nearly equivalent for planar molecules) the introduction of penetration integrals makes no significant difference in the predicted lowest $\pi^* \leftarrow \pi$, $S \leftarrow S$ and $T \leftarrow S$ transitions, variations amounting to

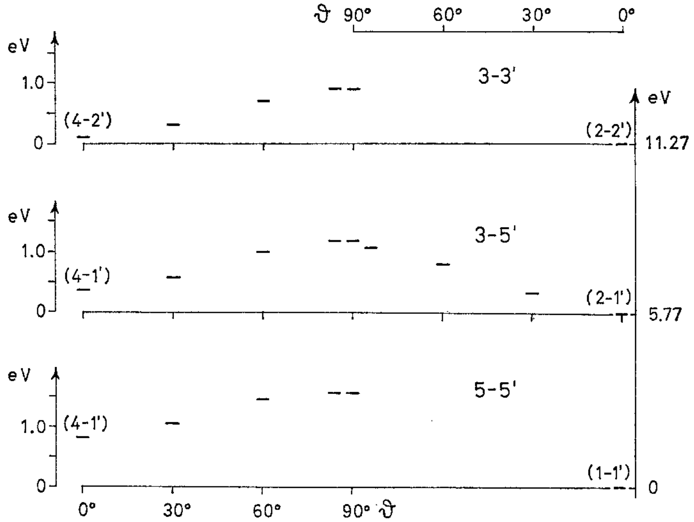

Fig. 4. Loss of total π-energy due to rotation of bis-oxadiazole rings with respect to one another. Calculated points are at 0°, 30°, 60°, 84° and 90°

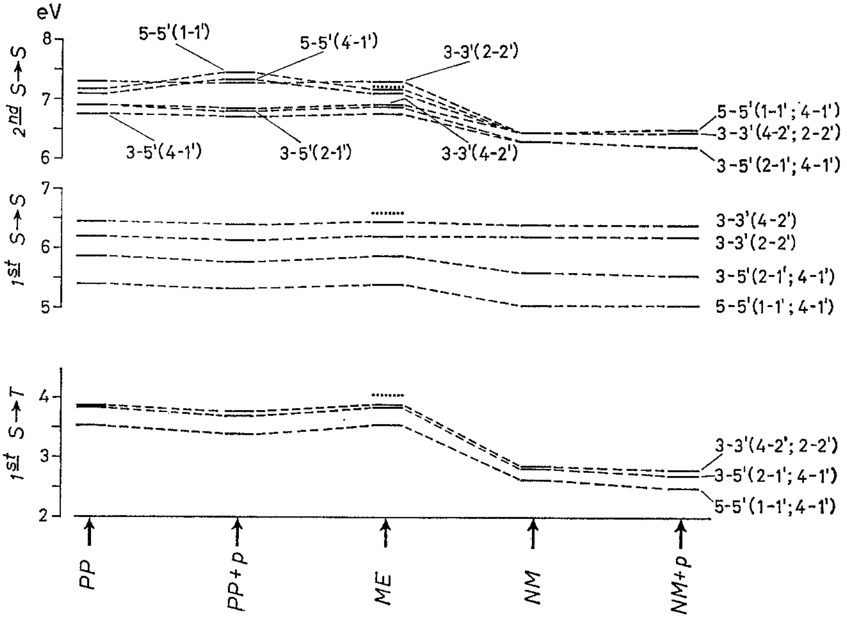

Fig. 5. Transition energies of bis-oxadiazoles calculated with different approximations (abscissa: PP, ME and NM refer to γ_{pq} integrals calculated according to Pariser-Parr, multipole expansion, and Nishimoto-Mataga procedures, respectively; $+p$ indicates that penetration integrals are included in the calculations)

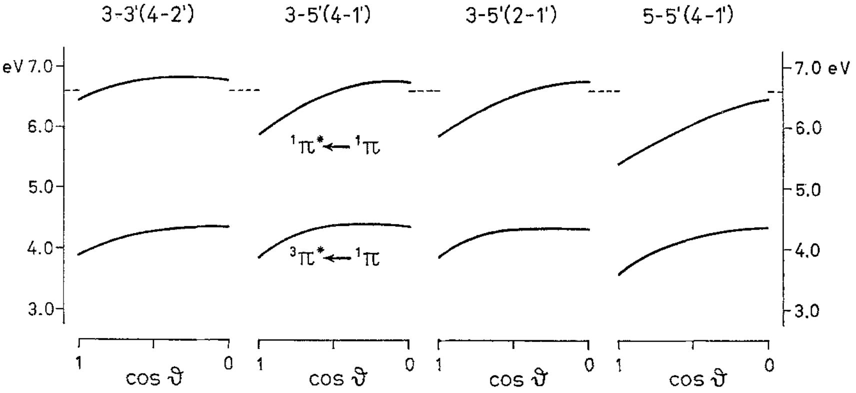

Fig. 6. Transition energies to lowest singlet and lowest triplet for different isomers of bis-oxadiazole as a function of the angle ϑ between the ring planes. The starting planar configuration is indicated on top of each plot

less than 0.1 eV. The NM procedure predicts most often [*1*, *10*] lower transition energies, but the calculated lowest $\pi^* \leftarrow \pi$, $S \leftarrow S$ for the different isomers seems not to depend on the choice of a particular approximation. The transition energies calculated for each of the two configurations of the 5-5′ and of the 3-5′ isomers differ from each other by 0.05 eV or less, whereas the 3-3′(2-2′) calculated transition is 0.25 eV lower than that of 3-3′(4-2′). The agreement of the predicted transition energy with the observed maximum absorption band can be considered satisfactory for 5-5′, the difference of the various calculations being within +0.20 (PP, ME) and −0.10 (NM) eV from the measured value, 5.17 eV [*7*]. The transition energy shift in going from 5-5′ to 3-3′ is also correctly predicted, because the latter's maximum absorption is > 6.0 eV [*7*]*.

The calculated pattern for the second $\pi^* \leftarrow \pi$ transition is entirely dependent on the procedure and no choice can be made at this stage of approximation.

The comparison of the calculated transitions with the available spectroscopic data was made on the assumption that the two oxadiazole rings of the dissolved molecules are coplanar. This point however is by no means certain, and our assignement of the coplanar arrangement as the favoured one (Fig. 4) derives mainly from the cos ϑ factor embodied in the β_{CC} integral. This is a fair approximation so far as the integral involves $2p\pi$ orbitals, and we have used it for evaluating the influence of rotation on the transition energies. As is shown in Fig. 6 the isomers are increasingly affected in the order 3-3′, 3-5′, 5-5′, and the lowest calculated transition for two perpendicularly bound oxadiazole rings is very near that of oxadiazole itself (dotted levels of Fig. 5), and even slightly larger for 3-3′ and 3-5′ isomers.

The influence of the configurational change on the charge distribution and bond orders of a given isomer is rather small and does not alter the general pattern

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* The lowest $\pi^* \leftarrow \pi$ transition is $B_1 \leftarrow A_1$ for C_{2v} and $B_u \leftarrow A_g$ for C_{2h} systems, both allowed, $\vec{x}$-(C–C bond)-polarized in the first, plane-polarized in the second case, and it is $B \leftarrow A$ for the non planar symmetric isomers. The bands of the recorded spectra [*7*] have $\varepsilon_{\max} > 10^4$.

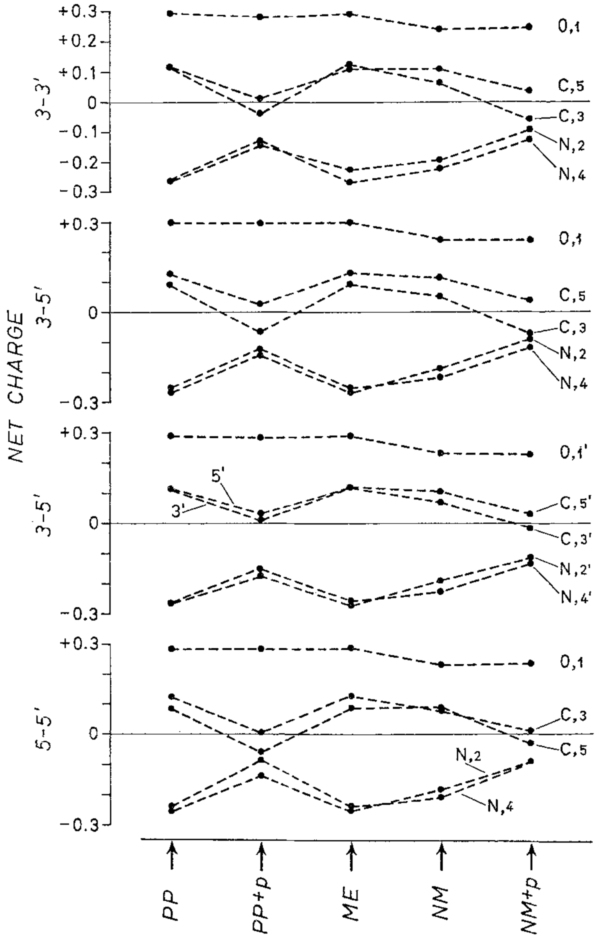

Fig. 7. Net π-charge on the planar bis-oxadiazoles calculated with different approximations (abscissa as in Fig. 5)

of the molecular diagram of that isomer. The largest changes were found for the charge q_4 in the 5-5′ and 3-5′ isomers when the penetration integrals were included in the calculations. The charge q_4 with the PP approximation is 1.092 in 5-5′(1-1′) and goes to 1.124 in 5-5′(4-1′), with the 0.032 e increase coming mainly from a reduction of q_1 and q_5. Using the same approximation, 3-5′(2-1′) has $q_4 = 1.125$, which becomes 1.169 for 3-5′(4-1′) with the increment being balanced by an almost equivalent reduction in q_2.

We shall discuss, therefore, in more detail the modifications of the molecular diagram in the different isomers by referring to the configurations which were found to have the largest E_π: 5-5′(1-1′), 3-5′(2-1′) and 3-3′(2-2′).

The net charges for the atoms of the heterocyclic rings plotted in Fig. 7 show several interesting features. First of all, the electron deficiency on the oxygen atom changes very little in the series of isomers, is not affected by the introduction of penetration integrals and is only 0.05 e lower when the NM procedure is used.

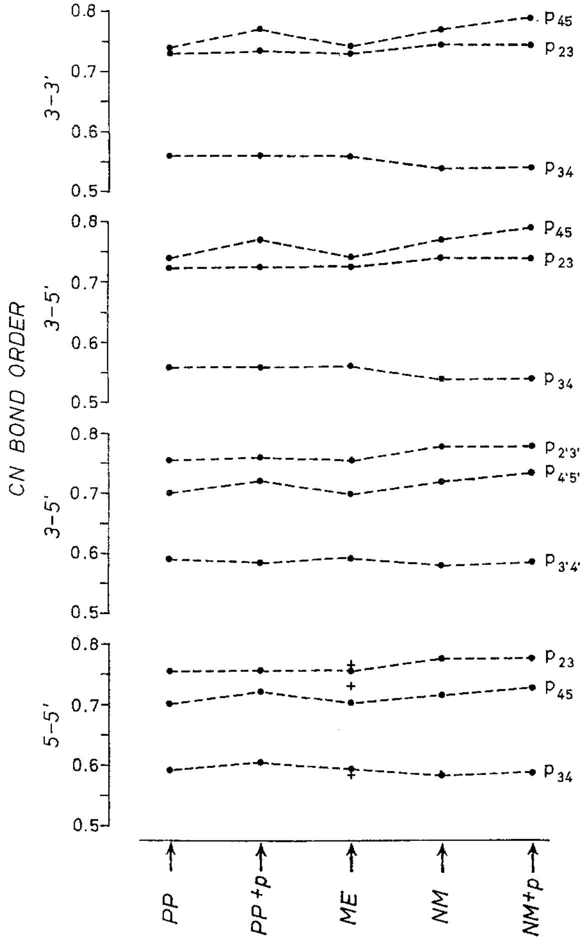

Fig. 8. C–N bond orders of the planar bis-oxadiazoles calculated with different approximations (abscissa as in Fig. 5). Crosses refer to unsubstituted oxadiazole

This NM lowering of the net charge seems a systematic one, because all the other atoms are affected in the same way.

The influence of penetration integrals is greatest on the net charge of carbon and nitrogen atoms where it brings in a reduction larger, in some cases, than 0.1. There is, as a consequence, a reversal of the polarity of the carbon atoms through which the two rings are joined, C_3 in 3-3' and C_5 in 5-5'. The 3-5' isomer presents an intermediate behaviour, with the reversal occurring for C_3 but not for $C_{5'}$ while the $C_{3'}$ atom acquires a very small net charge, ±0.01, depending on the use of the PP or NM procedure. The intermediate character of the 3-5' isomer with respect to the symmetric bis-oxadiazole is more apparent when the sequence of C–N bond orders is considered. This sequence (Fig. 8), which is $p_{23} > p_{45} \gg p_{34}$ with the 5-5' isomer (the same as found in oxadiazole itself), has p_{45} and p_{23} reversed with the 3-3' compound; in the 3-5' isomer each ring has a sequence equal to that of its particular type of substitution. If one regards the bond order

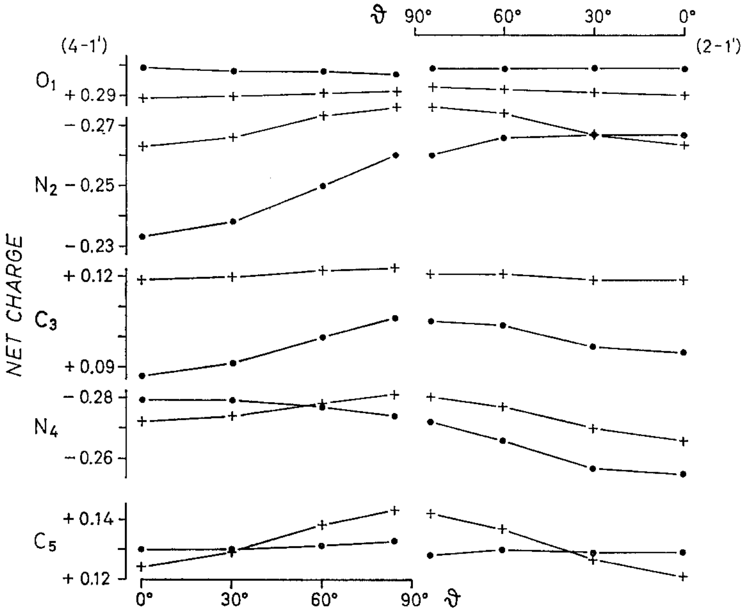

Fig. 9. Net π-charge on the atoms of 3-5'-bis-oxadiazole as a function of the angle ϑ between the ring planes. (Dots refer to the 3-substituted- and crosses to the 5-substituted-ring; configurations for $\vartheta = 0$ shown on top.) Calculated points are at 0°, 30°, 60° and 84°

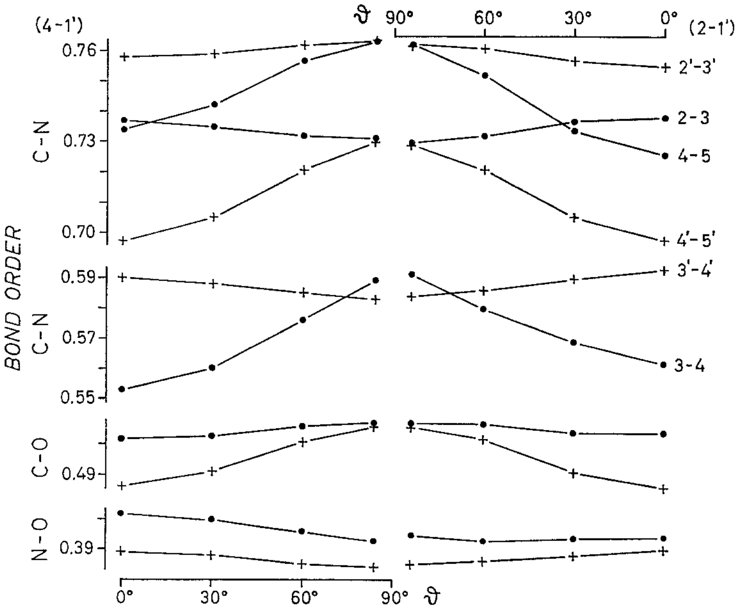

Fig. 10. Bond orders of 3-5'-bis-oxadiazole as a function of the angle ϑ between the ring planes. (Conventions as in Fig. 9.) Calculated points are at 0°, 30°, 60° and 84°

as a measure of equilibrium bond-length, then a correspondingly different sequence of C–N distances should be observed in the various isomers.

The distinctive properties which our calculation assigned to the two rings of 3-5′ bisoxadiazoles suggested an examination of the variations induced in the molecular diagram by the mutual rotation of the two rings around the C–C bond axis. The data are collected in Figs. 9 and 10 for charges and bond orders, where dots refer to the first ring (3 substituted) and crosses to the second. With the exception of oxygen, whose charge remains almost unaffected, the charges of the corresponding atoms of the two rings behave differently on rotation, especially for the nitrogen atoms which appear to be the most sensitive to the molecular configuration of the isomer [it should be remembered that the same rotation leads to different configurations for 3-5′(4-1′) and 3-5′(2-1′)]. Analogous remarks can be made concerning the bond orders, where C–O and N–O are much less affected than C–N bonds. And here the dependence of p_{34} and $p_{3'4'}$ on the rotation is remarkably different from that of the others: the first increases and the second decreases in a measure which reverses near 75° the sequence found in the planar configurations.

The question asked at the beginning about the influence of different approximation has been partly answered while examining the results on bis-oxadiazole. There will be a more detailed discussion after the case of other substituted oxadiazoles has been considered.

The Case of α-α'-Di-Diazolyl-Ethylenes

The geometry of these compounds was derived from that assumed for the bis-oxadiazoles by assigning a uniform bond length of 1.40 Å for the chain of carbon atoms joining the two rings, with the bond angles to the ethylene residue taken as 120°. It is obvious that in this case also three different isomers are possible according to whether the 3 or 5 positions are chosen for substituting the oxadiazole rings. Only the *trans* arrangement of each isomer was examined, since the *cis* arrangement would have the two rings at a distance much shorter than the van der Waals contact. Two different configurations of each *trans* isomer are possible depending on which atoms of each ring are on the same side of the central C–C chain. The identification of the different structures we have examined is made by stating which carbon atom of the ring is bound to the α or α' atom of ethylene and by specifying the adjacent ring atoms which are on the same side of the central C–C chain (Fig. 11). Thus α,5-α',5′(1-1′) corresponds to the structure formed by two 5-substituted oxadiazole rings with the oxygen atoms on the same side; when the first ring is rotated by 180° around its 5-α bond, the structure α,5-α',5′(4-1′) is obtained, which belongs to the C_{2h} symmetry group*.

Only α,3-α',3′ and α,5-α',5′ compounds have been reported [3] in the literature.

The discussion of our results will follow the same lines as for bis-oxadiazole. The pattern of the relative stabilities, defined as before, is shown in Fig. 12. The different isomeric configurations fall into the same order as the corresponding structures of bis-oxadiazoles, independently of the procedure chosen for γ_{pq} and of the introduction of $(A:pp)$ integrals. It is remarkable, however, that the E_π

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* It can be easily verified that α,3-α',3′(4-2′) also belongs to C_{2h} group. All the other structures are not symmetric.

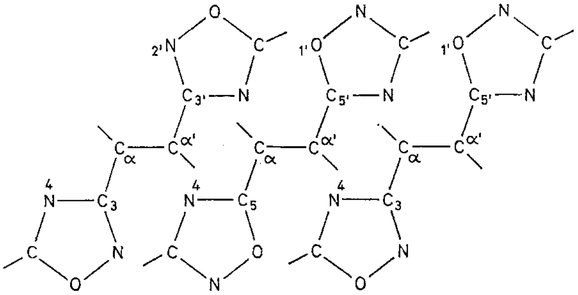

Fig. 11. Three configurations of *trans*-isomers of α-α'-di-diazolyl-ethylene. The other three configurations are obtained from them by rotation of 180° around the bond C(α')–C(*ring*)

energy difference between the two configurations of α,5-α',5′ is about twice the difference between the corresponding configurations of the α,3-α',5′ and α,3-α',3′ isomers. We cannot offer an explanation for this result which also places the α,5-α',5′(4-1′) configuration energetically closer to the α,3-α',5′ isomers than to its (1-1′) companion structure.

This fact has no influence on the predicted spectral behaviour of the two α,5-α',5′ configurations (Fig. 13), whose first $\pi^* \leftarrow \pi$, singlet-singlet are predicted

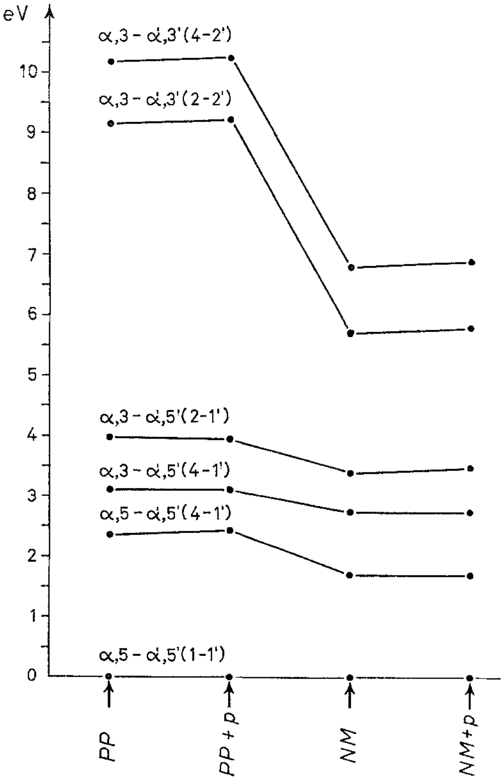

Fig. 12. Comparison of the total π-electron energy of α-α'-di-diazolyl-ethylene isomers

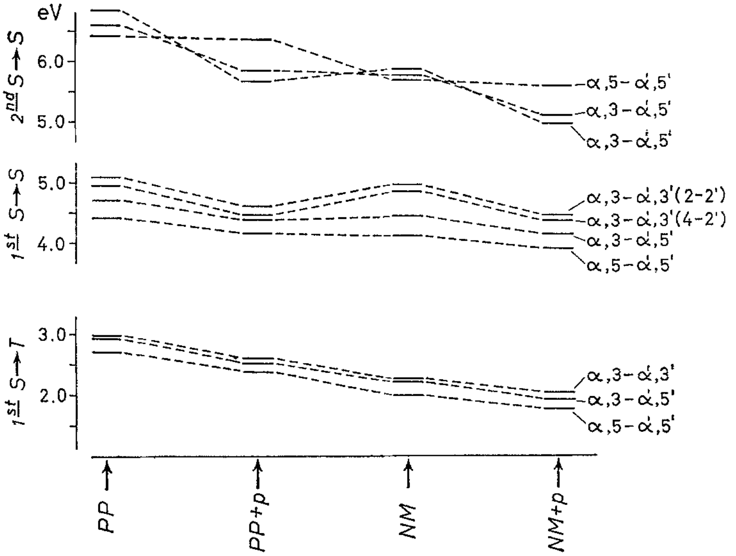

Fig. 13. Transition energies of α-α'-di-diazolyl-ethylenes calculated with different approximations (abscissa as in Fig. 5)

as being the same (within ±0.05 eV). A similar result is found for the α,3-α',5′ compounds, whereas a difference of 0.10—0.15 eV is predicted for the two configurations of the α,3-α',3′ isomer. As previously found, the PP procedure gives correspondingly higher transitions than the NM, with differences of about 0.5 eV. The comparison with the experimental results indicates that the simple PP procedure almost duplicates the observed absorption maxima, which are 4.40 and 5.10 eV, respectively, for α,5-α'5′ and α3-α'3′ isomers [7]. The simple NM prediction is not so good, but in both cases the introduction of penetration integrals makes the comparison of observed with the calculated transitions much worse. This is a rather surprising failure in view of what was found for bis-oxadiazoles, and a possible explanation could be that the observed spectra actually belong to non planar molecules. A small twisting of the assumed coplanar arrangement of the hetero-atomic rings would in fact shift the calculated transitions to higher energies, and therefore the predictions made with the inclusion of penetration integrals would be in better agreement with the spectra than those which neglect them.

The possibility of an out-of-plane ring twisting is in line with the very low bond orders calculated for the C–C bonds between the rings and the ethylene group, which would suggest a bond length greater than assumed in our model, perhaps between 1.45 and 1.50 Å.

The prediction for the second $\pi^* \leftarrow \pi$ transition appears to be entirely dependent on the approximations used for γ_{pq} and on the introduction of $(A:pp)$ integrals. The introduction of penetration integrals brings in an inversion of the order in the transition calculated without such integrals for the different isomers; the worst case is that of α,3-α',3′ which shows a difference of nearly 2 eV between the highest, PP, and the lowest, NM, prediction.

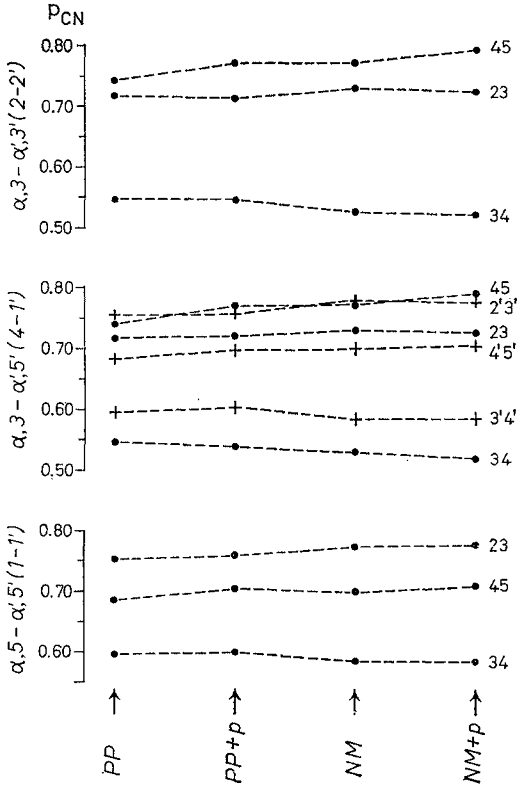

Fig. 14. C–N bond orders of some configurations of α-α'-di-diazolyl-ethylenes, calculated with different approximations. Dots refer to the first, and crosses to the second ring (abscissa as in Fig. 5)

The general appearance of the charge distribution and bond orders in the heteroaromatic rings is very similar to that previously examined for bis-oxadiazole. Fig. 14 gives the C–N bond orders which show that the substitution at carbon 3 brings in a reversion of p_{23} and p_{45} with respect to the unsubstituted or 5-substituted oxadiazole.

The charge distribution on the α and α' carbon atoms of the ethylene group has some interesting features. There is in general an electron migration towards the rings but its calculated value strongly depends on the chosen procedure, and is from five to ten times larger when (*A* : *pp*) integrals are included. The case of the non-symmetric compounds is shown in Fig. 15. Here the second ring (the one which is given primed numbers) always has a larger total π-electron population than the first. (The latter, according to the NM procedure, would actually show a 0.05 π-electron loss in some instances.) The largest π-electron migration is always from the atom α, and it seems therefore that each carbon atom has a tendency to contribute to the π-electron population of the ring to which it is *not* directly bound. [The α' carbon is even predicted as being negatively charged in some cases when (*A* : *pp*) integrals are neglected.]

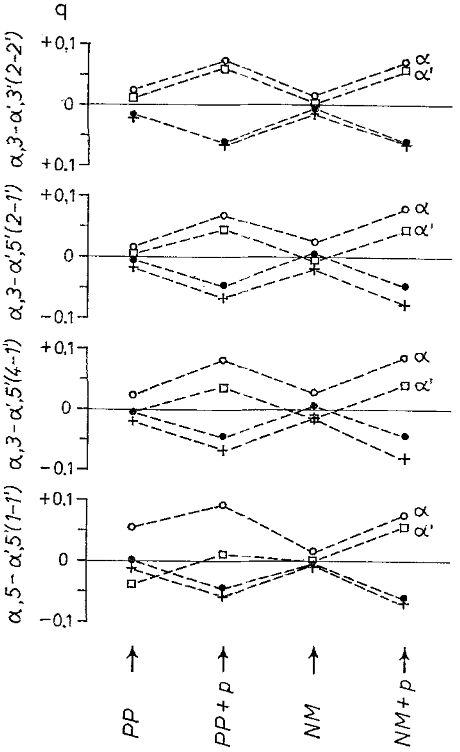

Fig. 15. Net charges on the α and α' carbon atoms for non-symmetric isomers, and total net charge migrated to each ring, calculated with different approximations (abscissa as in Fig. 5). Dots refer to the net charge of the first, and crosses to that of the second ring

Conclusions

The conclusive remarks about the results reported here will be made from two points of view: (i) the dependence of the predictions made on the choice of the approximation procedure; and (ii) the comparison of the predictions with the available experimental results.

(i) The calculated lowest $\pi^* \leftarrow \pi$, singlet-singlet, transition is scattered by ± 0.2 eV, depending on the approximation procedure adopted for γ_{pq} and $(A:pp)$. This is a large uncertainty considering that the range of the absorption maximum of a transition at 5 eV would be any value between 240—260 mμ. However, the set of results obtained with one given procedure can be reliably related to the lowest transition in the various compounds.

The prediction of the second $\pi^* \leftarrow \pi$ is, on the other hand, the most unreliable. The main reason for this situation might be the basis truncation at the four lowest monoexcited configurations which represents a convenient, but drastic, approximation. However, the NM choice for γ_{pq} seems to give, as a rule, values which are much too low for higher transitions.

The total π-electron energy appears to be a quantity that is very sensitive to even minor changes in a series of isomeric structures. It permits the different terms to fall into a succession which is independent of the choice of a particular procedure, and in the cases we have examined the isomeric configuration predicted as the most stable should be the one really present under normal experimental conditions.

The calculated π-electron distribution is strongly dependent on the introduction of penetration integrals. This is mainly due to their influence on the scaling of the diagonal elements of the energy matrix, through the evaluation of the core term [*1*, *2*]. The latter is a very delicate point and involves not only the penetration integrals (and the procedure for their evaluation), but also the choice of the valence state ionization potential of the atoms. We think that as far as semi-empirical techniques are needed in the theoretical study of large molecules, the choice of the *best* procedure should be made by comparison with experimental data. The most suitable should be [*2*] the dipole moment, and eventually the lowest singlet-triplet transition, but there is a regretable lack of data concerning these.

The sequence of bond orders is much less sensitive to the choice of γ_{pq} and $(A:pp)$ and should give a reliable prediction of the sequence of the bond lengths.

(ii) The weakest point of the oxadiazole ring, as predicted from the molecular diagrams we have calculated, is the N–O bond: it has the lowest bond order and is the largest local dipole in the molecule, N(−)–O(+), offering therefore the easiest point of attack for any reagent. The chemistry of oxadiazoles shows that the N–O bond is broken in both acid and alkaline hydrolysis, and also in the spontaneous isomerization of some simple derivatives [*3*].

Common electrophilic reactions do not take place at the carbon atom of monosubstituted oxadiazoles, whereas several nucleophilic reactions are described [*3*]. This behaviour is in agreement with our predictions which show that the C-3 and C-5 positions available for substitution reactions are always electron-deficient.

Comments about the comparison with the observed spectra have been made in the foregoing while discussing calculated transition energies. Here we wish to point out that the simultaneous presence in a solution of the two configurations of a given isomeric structure could possibly show up in the temperature dependence of absorption band intensities. The reported spectra of α,3-α',3'- and α,5-α',5'-di-diazolyl-ethylene show in fact a certain amount of structure [*7*] of the type usually related to vibrational coupling. Considering that our predicted band separations between different isomeric configurations are 0.05 to 0.15 eV it does not seem unlikely that the observed spectral structure could be due to both vibrational coupling and configuration mixing.

Concerning the so far unknown 3-5′ type oxadiazole derivatives, the maximum absorption bands are expected at an intermediate position between those found for 3-3′ and 5-5′ types; the chemical behaviour of each heteroaromatic ring should be similar to that shown by compounds with the same type of substitution.

Finally, it seems to us fair to state that predictions of the type we have made, obtained by a given procedure for a series of related isomeric molecules, compare favourably with the experimental results in such a measure as to represent a reliable tool for identifying and classifying the different isomers.

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Part of this work has been reported in a seminar at the NATO School for Theoretical Chemistry in Frascati (April 1965, M. C.) and in a lecture delivered at the University of Göttingen (May 1966, L. P.).

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Appendix

Calculation of the Basic Integrals

The calculated overlap integrals are: $S_{NO} = 0.1641$, $S_{CO} = 0.1548$, $S_{CN} = 0.2101$, $S_{CC} = 0.2439$.

The γ_{pq} integrals can be obtained according to the procedures we have described and are thus not listed here in order to save space.

The $(A:pp)$ integrals are given in Tab. A.1. They are indicated by a more compact notation which specifies the neutral atom and the atom bearing the $2p\pi$ orbital referring to the π-electron considered. Thus (N:CC), for a distance of 1.35 Å, groups together (2:33), (4:33), (4:55) etc. Me represents the neutral carbon atom of the methyl group. The line joining the A and p atoms was taken as the reference direction for evaluating each $(A:pp)$ integral.

Table A.1. *Penetration integrals*[a]

Integral	Distance	eV	Integral	Distance	eV
(C:CC)	1.40	1.009	(N:NN)	2.13	0.942
(C:CC)	2.20	0.047	(N:OO)	1.20	2.868
(C:CC)	2.42	0.019	(N:OO)	2.08	1.002
(C:NN)	1.35	1.195	(O:CC)	1.32	1.711
(C:NN)	2.12	0.053	(O:CC)	2.07	0.938
(C:NN)	2.48	0.011	(O:CC)	2.45	0.193
(C:OO)	1.32	1.300	(O:CC)	2.56	0.174
(C:OO)	2.07	0.053	(O:NN)	1.20	2.368
(C:OO)	2.45	0.009	(O:NN)	2.08	0.971
(N:CC)	1.35	1.893	(H:CC)	1.06	0.651
(N:CC)	2.12	0.916	(Me:CC)	1.52	0.657
(N:CC)	2.48	0.151	(Me:NN)	2.58	0.007
(N:CC)	2.58	0.137	(Me:OO)	2.56	0.006

[a] Integrals for distances larger than 2.7 Å have been neglected.

Eigenfunctions and Eigenvalues

Eigenvectors and eigenvalues are not given in order to avoid printing a large set of numerical data whose significance is essentially in their trend. This is given in the figures of the text and should be sufficient to warrant our conclusions. A tabulation of the data can be obtained by anyone interested upon request to the authors.

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