Theoret. chim. Acta (Berl.) 8, 117—127 (1967)

Multi-Conformational Compounds with Two Absorbing Groups. I

AMATZYA Y. MEYER
Institut de Biologie Physico-Chimique, 13, Rue Pierre Curie, Paris V

JOSIANE SERRE
Laboratoire de Chimie E.N.S.J.F. 24, Rue Lhomond, Paris V

Received April 20, 1967

A study of the mutual dependence of steric conformation and electronic properties is proposed for two-chromophore multi-conformational molecules. The first stage, a configurational-interaction study based on geometrical data, is described, and it is shown that although electronic transition energies do not differ much within a group of similar compounds, the nature of the electronic states does change with structure.

Une étude de l'interdépendance de la conformation stérique et des propriétés électroniques des composés à conformations multiples à deux chromophores, est abordée par des calculs d'interaction de configuration. On montre que dans un tel groupe de composés, c'est plutôt la nature des transitions électroniques que leur énergie qui varie selon la structure.

Es wird eine Studie über die wechselseitige Abhängigkeit von sterischer Konformation und Elektroneneigenschaften für Moleküle mit Mehrfach-Konformation bei zwei Chromophoren angestellt. Als erster Schritt wird eine auf geometrischen Daten basierende Konfigurationswechselwirkungsstudie beschrieben und es wird gezeigt, daß die Natur der Elektronenzustände sich mit der Struktur ändert, obwohl die Elektronenanregungsenergien in einer Gruppe ähnlicher Verbindungen nicht stark voneinander abweichen.

1. Introduction

Many examples are known [*1*] of unconjugated two-chromophore compounds in which physical properties, such as ultraviolet spectra, are not a simple superposition of the separate chromophore properties. The modifications, variously attributed to "no bond resonance" [*2*], "interaction through space" [*3*], or "spectroscopic interaction" [*4*], are now currently considered [*5*] in terms of "charge transfer" [*6*] theories. Nature of the groups apart, the phenomena obviously depend upon the geometry of the molecule — that is, upon the mutual position (distances, angles) of the atoms in the two absorbing moieties.

The complex nature of the geometrical factor may be illustrated by the case of molecules, such as bicyclo [2.2.2.] oct-5-en-2-one [*7*], which contain a carbonyl and double bond, unconjugated (in the classical sense) but suitably oriented in space to permit some interaction; this may be manifested by the appearance, at 200—210 mμ, of an absorption band, interpreted as due to charge-transfer from the double bond to the carbonyl, and by intensification and shifting of the ketonic $n \to \pi^*$ band, brought about by interaction with the charge-transfer configuration.

It has been stated [*8*, *9*] that the amount of interaction depends on the magnitude of overlap between the relevant orbitals; the various interactions may thus be differently influenced by geometry: the oxygen non-bonding and π-bonding orbitals being orthogonal, they do not necessarily achieve, at the same time, overlaps of equal importance with other orbitals of the molecule.

The intensity of the $n \rightarrow \pi^*$ transition may be augmented by an interaction with a charge-transfer band directed either from the double bond to the carbonyl, or from the carbonyl to the double bond [*7*, *9*, *10*]. When these two groups are coplanar, that is, have their π-orbitals parallel, the $n \rightarrow \pi^*$ transition is optimally disposed to interact with a carbonyl to double-bond transfer, but the intensity — and hence, the energy to be borrowed from such transfer — is minimal. The intensity of the double bond to carbonyl transfer is high, but the possibility of interaction is poor. When the two groups are perpendicular, it is just the opposite situation that prevails. Thus, very little can be said without actual calculation for the usually encountered conformations which are intermediate.

In what follows, we approach such a calculation by first proposing a simple semiempirical configurational-interaction (CI) scheme [*5*, *11*] to evaluate intramolecular two-chromophore interactions; the spatial relationships of the two groups are accounted for in a simple way. The molecule is regarded as consisting of two parts, each having either donor or acceptor properties, such that there exist some excited configurations in which an electron has been intramolecularly transferred from one part to the other. The ground state of the unified molecule, with energy taken as zero, is that in which the various electrons are distributed in the orbitals they occupy in the ground states of the separated parts; locally excited configurations of the overall system are constructed by extension of the corresponding states in the isolated chromophores. A scheme for integral evaluation is suggested, the terms of the CI matrix are calculated, and the matrix diagonalized. The relative amount of local or transfer excitation are thus assigned to the spectral bands.

The method is here presented as applied to "phenyl-carbonyl" compounds, that is, ketones substituted by a phenyl-group, the $C=O$ and C_6H_5 being separated by a chain of single bonds. Many examples of such compounds, which present an "abnormal" spectrum are known (1, 2). In these molecules, both the phenyl to carbonyl and the carbonyl to phenyl charge-transfers are possible; it is the detailed structure of the molecule, including the rotation state of benzene about its axis of attachment, which determines the influence of each transfer direction upon the overall spectrum.

Experimentally, the three ultraviolet absorption bands of benzene occur at 178 mμ ($f = 1.035$, $\log \varepsilon = 4.7$), 201 mμ ($f = 0.126$, $\log \varepsilon = 3.8$) and 253 mμ ($f = 0.01$, $\log \varepsilon = 2.3$) [*9*, *12*]. Acetaldehyde vapour has a $\pi \rightarrow \pi^*$ transition [*13*] at 167 mμ ($f = 0.13$, $\log \varepsilon = 4.3$), and a band at 182 mμ ($f = 0.037$, $\log \varepsilon = 4.0$). The carbonyl transition, considered [*14*] as the symmetry-forbidden $n \rightarrow \pi^*$, is at about 280 mμ, with a molar extinction coefficient that rarely exceeds $\varepsilon = 30$ for "normal" cases (for acetone, $\varepsilon < 10$). A compound carrying non-interacting phenyl and carbonyl groups would therefore have, besides the 160—170 mμ and the intense 180 mμ bands, a strong 200 mμ ($\log \varepsilon \sim 3.8$) and weaker 250 mμ ($\log \varepsilon \sim 3.2$) aromatic absorptions, and a very weak ketonic band at about 280 mμ.

The other extreme, that of a carbonyl directly linked to phenyl, may be illustrated by acetophenone [*15*] (spectrum in heptane solution): the aromatic bands are shifted and intensified, lying at 238 mμ (log $\varepsilon = 4.10$) and 279 mμ (log $\varepsilon = 2.95$), the ketonic band displaced to 320 mμ, almost without intensification (log $\varepsilon = 1.61$).

The "abnormal" phenyl-carbonyl coumpounds, which have common features with both extremes, may be characterized by shifted and augmented benzene –250 mμ and carbonyl –280 mμ bands. Thus, 2-phenylcyclohexanone [*3*] absorbs at 260 mμ (log $\varepsilon = 2.3$), and at 290 mμ (log $\varepsilon = 1.6$) (in cyclohexane), 1,1-diphenylbutanone [*3*] at 260 mμ (log $\varepsilon = 2.7$), at 290 mμ (log $\varepsilon = 2.4$) and 3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one [*16*] (see formula C) at 259—271 mμ (log $\varepsilon = 2.5$) and at 288—320 mμ (log $\varepsilon = 2.2$—2.5).

2. Method of Calculation

The method was constructed by application to the benzene molecule, one of the two constituting parts of phenyl-carbonyl compounds.

Within the frame of σ-π separation, and in view of a LCAO approach, six atomic orbitals $\chi_a, \chi_b, \chi_c, \chi_d, \chi_e, \chi_f$, centered on the benzene atoms a, b, c, d, e, f, are needed. These were chosen as Slater $2p$ orbitals, but overlap integrals were assumed null. From the six benzene LCAO orbitals, with coefficients determined uniquely by D_{6h} symmetry [*17*], the first five, $\varphi_1 \ldots \varphi_5$ by increasing energy, will be needed. They are considered as orthonormal. Anticipating work on the more complex unified molecules, no further usage of symmetry is to be done; φ_2 and φ_3, φ_4 and φ_5, are regarded as distinct. Naturally, the effects of symmetry, to the amount that they persist, are reflected in the results.

A ground state Ψ_0 and four monoexcited configurations, $\Psi_1 \ldots \Psi_4$, were formulated and energy expressions $E_{ij} = \int \Psi_i H \Psi_j d\tau$ written down with the total π-Hamiltonian H. The diagonal terms E_i^0 are the differences $E_{ii} - E_{00}$; most of the off-diagonal terms, except E_{14} and E_{23} are zero (Tab. 1).

The scheme for evaluation of atomic integrals neglects all bi- or polyelectronic integrals, other than the Coulomb repulsion terms (pp, rr) which are calculated analytically, and used for the Coulomb α_p integrals; the resonance integrals, β_{pr}, are fixed so that the ensemble reproduce experimental energies.

As regards bielectronic integrals, it is the overlap-nullity hypothesis

$$\int \chi_p \chi_q d\tau = 0 \tag{1}$$

that suggests the zero differential-overlap (ZDO) approximation [*18*]

$$(pq, rs) = \delta_{pq} \delta_{rs}(pp, rr) \tag{2}$$

that is, all charge distributions $\chi_p \chi_q$, with $p \neq q$, occurring in bielectronic integrals, are considered negligeable.

In fact, since LÖWDIN has shown that orthogonalized atomic orbitals (OAO's) defined to satisfy Eq. (1) will also satisfy approximately Eq. (2), it has been variously argued [*18, 19, 20*], that non-orthogonal Slater orbitals may sometimes be considered equivalent to OAO's: Eq. (1) postulated, Eq. (2) concluded. This is strictly true for cases where LCAO coefficients are determined uniquely by symmetry, when calculations based on non-orthogonal orbitals or on OAO's are equivalent step-by-step, and always true to a first order in S for other cases. In fact, (pq, rs) integrals to occur in calculations for the elaborate unified molecule may be approximated by a Mulliken-type relation,

$$(pq, rr) = \tfrac{1}{2} S_{pq}[(pp, rr) + (qq, rr)]$$

and are then seen to be small, because of feeble overlap, and usually negligeable, for they appear in sums containing high-value quantities.

As it is known [*21*] that values of Coulomb repulsion integrals [*22*] based on Slater's effective charges are overestimated, probably due to disregard of correlation effects, Z was readjusted semiempirically. The bielectronic monocentric integral is first described in terms of the ionization potential W_p and electro-affinity A_p [*23, 24*]

$$(pp, pp) = W_p - A_p - \varepsilon(W_p + A_p)$$

where the corrective factor ε accounts for the effective charge difference between the neutral atom and its derived ion. With $\varepsilon = 0.110$ [*23*], one gets for carbon (CC, CC) = 9.87 eV. Next we derive (CC, CC) = 5.324 Z, and get $Z_C = 1.854$, which is the value to be used.

For the monoelectronic monocentric integrals, α_p, the usual relation [*25*]

$$\alpha_p = W_p - \sum_{\substack{q \text{ or } Q \\ \neq p}} \{(Q\!:\!pp) + n_Q[(pp, qq) - \tfrac{1}{2}(pq, qp)]\}$$

was used. The penetration integrals $(S\!:\!pp)$ are neglected [*25*]. n_Q is the number of electrons, in orbitals of the same symmetry as the appropriate orbital on P, contributed by atom Q to the conjugated system.

We are left with the resonance integrals, β_{pq}, which have to satisfy certain demands. First, we would like them to compensate, to a certain measure, for approximations introduced up to now; they should be adjusted by concurrent use of non-approximate equations and experimental data. Second, they should be written as some function of the interatomic distance, because we will have to estimate them in the general ease of the unified molecule: the approximation

$$\beta_{p,r} = 0 \qquad p, r \text{ non-neighbours}$$

usually made whenever Eq. (2) is accepted [*18*] cannot be retained in the present case, because β-integrals appear by themselves, never together with high value quantities of another nature; they cannot be neglected. Thirdly, they should fall into one of the accepted schemes for their evaluation.

Accordingly, we begin with [*26*]

$$\beta_{pq} = \tfrac{1}{2} k\, S_{pq}(\alpha_{pp} + \alpha_{qq})$$

where S_{pq} is the desired function of distance; all α-integrals in benzene being equal, this reduces to

$$\beta_{pq} = kS_{pq}\,. \tag{4}$$

The necessary overlap and Coulomb repulsion integrals are now calculated, Eq. (4) put in the expressions developed for benzene electronic transitions in terms of OAO's [*27*], and a suitable value found for k: it is $k = -10.14$.

It rests to ask for the signification of such β integrals, calculated from an orthonormalized scheme by the measure of their non-orthogonality. It has been shown [*25*] that when β_{pq} integrals over non-orthogonal orbitals are expressed as a corrected Mulliken relation

$$\beta_{pq} = \tfrac{1}{2}\, S_{pq}(\alpha_p + \alpha_q) + \varepsilon_{pq}$$

then the orbitals normalized and resonance integrals recalculated, they are equal — to first order in S — to the corrective terms ε_{pq}. Having made the supposition expressed by Eq. (1), we may consider our β values not as the monoelectronic-bicentric integrals themselves, but as the difference between them and their approximated Mulliken value. If this is true, we may note, their sign is not necessarily negative.

When treating later the unified molecule of a phenyl-carbonyl compound, a further approximation will be made: although the constant k contains α-integrals, which depend somewhat upon environment, Eq. (4) will be taken as definitive, and the k-value as general.

The scheme is thus complete; to test for its coherence, numerical values of the benzene CI matrix are calculated and the matrix diagonalized (Tab. 1): eigenvalues and oscillator strengths are satisfactory.

Table 1

Configurations

$$\Psi_0 = (\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2\varphi_3\overline{\varphi}_3)$$
$$\Psi_1 = 2^{-1/2}\,[\varphi_1\overline{\varphi}_1(\varphi_4\overline{\varphi}_2 - \overline{\varphi}_4\varphi_2)\,\varphi_3\overline{\varphi}_3]$$
$$\Psi_2 = 2^{-1/2}\,[\varphi_1\overline{\varphi}_1(\varphi_5\overline{\varphi}_2 - \overline{\varphi}_5\varphi_2)\,\varphi_3\overline{\varphi}_3]$$
$$\Psi_3 = 2^{-1/2}\,[\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2(\varphi_4\overline{\varphi}_3 - \overline{\varphi}_4\varphi_3)]$$
$$\Psi_4 = 2^{-1/2}\,[\varphi_1\overline{\varphi}_1\varphi_2\overline{\varphi}_2(\varphi_5\overline{\varphi}_3 - \overline{\varphi}_5\varphi_3)]$$

CI–MO's

$$\Theta_0 = 0 \qquad E_0^0 = 0$$
$$\Theta_1 = 2^{-1/2}\,(\Psi_1 - \Psi_4), \quad E_1^0 = 4.80\text{ eV},\ f_{0\to 1} = 2.5.10^{-4}$$
$$\Theta_2 = 2^{-1/2}\,(-\Psi_2 + \Psi_3), \quad E_2^0 = 5.72\text{ eV},\ f_{0\to 2} = 0.8$$
$$\Theta_3 = 2^{-1/2}\,(\Psi_2 + \Psi_3), \quad E_3^0 = 6.05\text{ eV},\ f_{0\to 3} = 4.10^{-4}$$
$$\Theta_4 = 2^{-1/2}\,(\Psi_1 + \Psi_4), \quad E_4^0 = 6.95\text{ eV},\ f_{0\to 4} = 1.15$$

The foregoing notions are now used to consider the carbonyl group. Three atomic orbitals are introduced: χ_g and χ_h, Slater orbitals on the ketonic carbon and oxygen, respectively, and χ_H — the $2p_y$ non-bonding oxygen orbital. From these, the bonding φ_7, antibonding φ_8 and non-bonding φ_9 molecular orbitals are constructed (Tab. 2) with coefficients r and s to be determined by an SCF approach.

The monocentric $(\chi_h\chi_h, \chi_h\chi_h) = (\chi_H\chi_H, \chi_H\chi_H)$ is evaluated [*24*, *28*], with [*23*] $\varepsilon = 0.084$, and found 13.66 eV, from which $Z_0 = 2.566$. Other bielectronic integrals are calculated [*22*] with interatomic distances 1.21 Å or zero, as appropriate. These, together with formulas and values for the monoelectronic Coulomb integrals, are given in Tab. 2.

In order to be later able to test our r, s and β_{CO} values, three possible configurations are now considered: a ground state with orbitals φ_7 and φ_9 doubly occupied, and two excited states, Ψ_5 corresponding to the carbonyl $\pi \to \pi^*$ transition, Ψ_6 — to its $n \to \pi^*$ transition. Calculating their energies and substracting the expression for ground state energy, the expressions for the two transition energies, $E^0_{\pi\to\pi^*}$ and $E^0_{n\to\pi^*}$ are obtained.

Table 2

$$\varphi_7 = r\,\chi_g + s\,\chi_h$$
$$\varphi_8 = s\,\chi_g - r\,\chi_h$$
$$\varphi_9 = \chi_{\mathrm{H}}$$
$$\Psi_5 = 2^{-1/2}\,[(\varphi_8\bar{\varphi}_7 - \bar{\varphi}_8\varphi_7)\,\varphi_9\bar{\varphi}_9]$$
$$\Psi_6 = 2^{-1/2}\,[\varphi_7\bar{\varphi}_7(\varphi_8\bar{\varphi}_9 - \bar{\varphi}_8\varphi_9]$$
$$(gg, hh) = 8.40\ \mathrm{eV},\ (gg, \mathrm{HH}) = 7.90\ \mathrm{eV}$$
$$(hh, \mathrm{HH}) = 12.19\ \mathrm{eV},\ (h\mathrm{H}, \mathrm{H}h) = 0.73\ \mathrm{eV}$$
$$\alpha_g = W^0_{2px} - (gg, hh) - 2(gg, \mathrm{HH})$$
$$\alpha_h = W^0_{2px} - (gg, hh) - 2(hh, \mathrm{HH}) + (h\mathrm{H}, \mathrm{H}h)$$
$$\alpha_{\mathrm{H}} = W^0_{2py} - (gg, \mathrm{HH}) - (hh, \mathrm{HH}) - (\mathrm{HH}, \mathrm{HH}) + \tfrac{1}{2}\,(h\mathrm{H}, \mathrm{H}h)$$
$$E^0_5 = (s^2 - r^2)\,(W^{\mathrm{C}}_{2px} - W^{\mathrm{O}}_{2px}) - 4rs\beta_{\mathrm{CO}} + (1 - 6r^2s^2)\,(gg, hh) + \\ + (2r^2s^2 - r^4)\,(gg, gg) + (2r^2s^2 - s^4)\,(hh, hh)$$
$$E^0_6 = s^2W^{\mathrm{C}}_{2px} + r^2W^{\mathrm{O}}_{2px} - W^{\mathrm{O}}_{2py} - 2rs\beta_{\mathrm{CO}} + r^2s^2[(gg, gg) + \\ + (hh, hh)] + (r^4 + s^4)\,(gg, hh) - r^2(gg, \mathrm{HH}) - s^2(hh, \mathrm{HH}) + \\ + (r^2 + \tfrac{1}{2})\,(h\mathrm{H}, \mathrm{H}h)$$

Hückel: $r = 0.5969$, $s = 0.8023$
SCF: $r = 0.5649$, $s = 0.8251$

To find suitable values for r, s and β_{CO}, we begin with a Hückel calculation of r and s [*29*], then effect several SCF treatments (zero overlap and differential overlap), each with its own β-value, and test whether the resulting r and s yield acceptable values for $E^0_{n\to\pi^*}$ and $E^0_{\pi\to\pi^*}$. The best run was with $\beta_{\mathrm{CO}} = -3.3$ eV; then transition $n \to \pi^*$ at 300 mµ, $f = 0$, transition $\pi \to \pi^*$ at 145 mµ, $f = 0.39$ (experimentally [*30*] 304 mµ, and 156 mµ with $f = 0.1$—0.5 [*31*]). Using now Eq. (4), we get, for carbon π-orbital paired with oxygen π-orbital, $k = -15.07$; again, this value is considered constant. β-Integrals between carbon π-orbitals and oxygen n-orbitals, *when perpendicular*, are null,

$$\beta_{p,\mathrm{H}}(p \perp \mathrm{H}) = 0\,. \tag{5}$$

3. Application to Phenyl-Carbonyl Compounds

Electronic states for compounds which contain both a phenyl and a carbonyl group are described in terms of nine atomic orbitals: the six benzene π-orbitals $\chi_a, \ldots \chi_f$, and the three ketonic χ_g, χ_h and χ_{H}. The molecular orbitals are assumed to be the original separate-molecule functions, $\varphi_1, \ldots \varphi_5$ of the benzene, φ_7, φ_8, φ_9 of carbonyl. In the ground state Ψ_0 of the unified molecule, orbitals φ_1, φ_2, φ_3, φ_7 and φ_9 are doubly occupied. Configurations resulting from local excitations are described by extension of the determinants $\Psi_1, \ldots \Psi_6$, to include the supplementary orbitals, e.g.

$$1/\sqrt{2}\,[\varphi_1\bar{\varphi}_1(\varphi_4\bar{\varphi}_2 - \bar{\varphi}_4\varphi_2)\,\varphi_3\bar{\varphi}_3\varphi_7\bar{\varphi}_7\varphi_9\bar{\varphi}_9]$$

replacing

$$\Psi_1 = 1/\sqrt{2}\,[\varphi_1\bar{\varphi}_1(\varphi_4\bar{\varphi}_2 - \bar{\varphi}_4\varphi_2)\,\varphi_3\bar{\varphi}_3]\,.$$

In addition, four charge-transfer states are formed, Ψ_7 and Ψ_8 from phenyl to carbonyl, Ψ_9 and Ψ_{10} — in the reverse direction (Tab. 3). It will be later shown, by an example, that inclusion of the last two, of high energy and feeble interactions, does not affect the results; they are not included in the calculations of Tabs. 4 and 5.

Table 3

$$\begin{aligned}
\Psi_7 &= 2^{-1/2}\,[\varphi_1\bar{\varphi}_1(\varphi_8\bar{\varphi}_2 - \bar{\varphi}_8\varphi_2)\,\varphi_3\bar{\varphi}_3\varphi_7\bar{\varphi}_7\varphi_9\bar{\varphi}_9]\\
\Psi_8 &= 2^{-1/2}\,[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2(\varphi_8\bar{\varphi}_3 - \bar{\varphi}_8\varphi_3)\,\varphi_7\bar{\varphi}_7\varphi_9\bar{\varphi}_9]\\
\Psi_9 &= 2^{-1/2}\,[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3(\varphi_4\bar{\varphi}_7 - \bar{\varphi}_4\varphi_7)\,\varphi_9\bar{\varphi}_9]\\
\Psi_{10} &= 2^{-1/2}\,[\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\varphi_3\bar{\varphi}_3(\varphi_5\bar{\varphi}_7 - \bar{\varphi}_5\varphi_7)\,\varphi_9\bar{\varphi}_9]
\end{aligned}$$

For a planar conformation, that is, when the phenyl and carbonyl have all their π-orbitals parallel, the CI matrix elements may now be written. We note, however, that because of Eqs. (2) and (5), the interaction between the carbonyl $n \rightarrow \pi^*$ transition Ψ_6 and all other configurations is zero, for example,

$$\begin{aligned}
\langle\Psi_0 \mid H \mid \Psi_6\rangle = \sqrt{2}\,[I_{89} + 2(\varphi_1\varphi_1, \varphi_8\varphi_9) + 2(\varphi_2\varphi_2, \varphi_8\varphi_9) + \cdots\\
- (\varphi_1\varphi_9, \varphi_8\varphi_1) - \cdots - (\varphi_7\varphi_9, \varphi_8\varphi_7)] = 0\,.
\end{aligned}$$

As a consequence, the calculated shifts of the $n \rightarrow \pi^*$ bands are too large. For *the planar case* this cannot be improved within the frame of the ZDO approximation.

On diagonalisation of the CI matrix, eigenvalues and eigenvectors, which serve to calculate oscillator strengths, are found. Eigenvalues and f-values, together with the percentage of the most important contributing structures, are given in Tabs. 4 and 5 for two trial planar conformations A and B (Fig. 1). In spite of the geometrical similarities, some differences, which may reflect general trends, are noted. These are briefly discussed later.

Our next stage is to admit non-planarity of the phenyl-carbonyl system, and to calculate bi- and monoelectronic integrals for this general case.

Interatomic distances and bond angles, known or inferred, are used to estimate the geometry of the molecule within a coordinate system $[xyz]$. Then for each pair of atoms AB, a secondary bicartesian coordinate system [22] $[\xi, \eta, \zeta_A; \xi, \eta, \zeta_B]$ with A and B as origins, is constructed. Atomic orbitals on A and B are written as sums of orbitals directed along ξ, η, and ζ.

$$\chi_a = A_{ai}\,\chi_a + A_{aj}\,\chi_a + A_{ak}\,\chi_a$$

where the A's may be considered as the cosines between the axis of the $2p$ orbital and ξ, η or ζ.

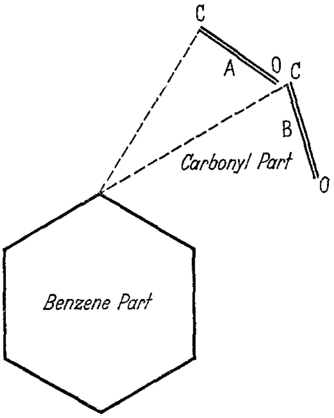


Fig. 1

Table 4. *Trial Conformation* A

Coordinates

$A(0.00, 1.40)$, $B(1.23, 0.70)$, $C(1.23, -0.70)$, $D(0.00, -1.40)$,
$E(-1.23, -0.70)$, $F(-1.23, 0.70)$, $G(1.36, 3.62)$, $H(2.38, 2.92)$

Eigenvalue (eV)	Transition Band (mμ)	f	Important Contributors	Description
-0.0081			$>99\%\ \Psi_0$	GS
4.7988	258	$2.1.10^{-4}$	$\sim 50\%\ \Psi_1$, $\sim 50\%\ \Psi_4$	BLE
5.6782	218	$8.31.10^{-1}$	$31\%\ \Psi_2$, $67\%\ \Psi_3$	
6.0536	204	$3.40.10^{-2}$	$68\%\ \Psi_2$, $32\%\ \Psi_3$	
6.9334	178	1.007	$48\%\ \Psi_1$, $49\%\ \Psi_4$	
7.4383	166	$9.49.10^{-2}$	$60\%\ \Psi_7$, $31\%\ \Psi_8$, $4\%\ \Psi_5$	PCCT
7.7709	159	$1.42.10^{-2}$	$33\%\ \Psi_7$, $66\%\ \Psi_8$	
8.3693	147	$7.60.10^{-1}$	$92\%\ \Psi_5$, $1.5\%\ \Psi_7$, $5\%\ \Psi_8$	CLE
(3.62)	(341)			$n \rightarrow \pi^*$

GS = Ground State
BLE = Benzene Local Excitation
PCCT = Phenyl to Carbonyl Charge Transfer
CLE = Carbonyl Local Excitation

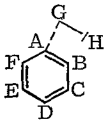


Table 5. *Trial Conformation* B

Coordinates

$A(0.00, 1.40)$, $B(1.23, 0.70)$, $C(1.23, -0.70)$, $D(0.00, -1.40)$
$B(-1.23, -0.70)$, $F(-1.23, 0.70)$, $G(2.55, 2.84)$, $H(2.88, 1.64)$

Eigenvalue (eV)	Transition Band (mμ)	f	Important Contributors	Description
-0.0117			$>99\%\ \Psi_0$	GS
4.7963	257	$2.8.10^{-3}$	$\sim 50\%\ \Psi_1$, $\sim 50\%\ \Psi_4$	BLE
5.6452	219	$8.85.10^{-1}$	$28\%\ \Psi_2$, $70\%\ \Psi_3$	
6.0526	204	$5.43.10^{-2}$	$69\%\ \Psi_2$, $29\%\ \Psi_3$	
6.8946	179	$9.21.10^{-1}$	$13\%\ \Psi_7$, $21\%\ \Psi_8$	BLE + PCCT
7.0188	176	$1.73.10^{-2}$	$31\%\ \Psi_1$, $29\%\ \Psi_4$ $13\%\ \Psi_7$, $39\%\ \Psi_8$ $18\%\ \Psi_1$, $20\%\ \Psi_4$	
7.5314	164	$1.56.10^{-2}$	$69\%\ \Psi_7$, $30\%\ \Psi_8$	PCCT
8.5148	145	$7.59.10^{-1}$	$86\%\ \Psi_5$, $3\%\ \Psi_7$ $8\%\ \Psi_8$	CLE + PCCT
(3.63)	(341)			$n \rightarrow \pi^*$

A Coulomb repulsion integral $(\pi_a\pi_a, \pi_b\pi_b)$ breaks thus down into a sum of eighty-one integrals, which may be grouped as

$$\begin{aligned}(\chi_a\chi_a, \chi_b\chi_b) = {} & (\sigma_a\sigma_a, \sigma_b\sigma_b) \times (A^2_{ak}A^2_{bk}) + \\ & + (\pi_a\pi_a, \pi_b\pi_b) \times (A^2_{ai}A^2_{bi} + A^2_{aj}A^2_{bj}) + \\ & + (\pi_a\pi_a, \bar{\pi}_b\bar{\pi}_b) \times (A^2_{ai}A^2_{bj} + A^2_{aj}A^2_{bi}) + \\ & + (\pi_a\pi_a, \sigma_b\sigma_b) \times (A^2_{ai}A^2_{bk} + A^2_{aj}A^2_{bk} + A^2_{ak}A^2_{bi} + A^2_{ak}A^2_{bj}) + \\ & + (\pi_a\bar{\pi}_a, \pi_b\bar{\pi}_b) \times (4A_{ai}A_{aj}A_{bi}A_{bj}) + \\ & + (\pi_a\sigma_a, \pi_b\sigma_b) \times [4A_{ak}A_{bk}(A_{ai}A_{bi} + A_{aj}A_{bj})] \,.\end{aligned}$$

Table 6. *Structure* C

Coordinates

$A(-1.336, 0.698, 0)$, $B(-2.546, 1.397, 0)$, $C(-3.755, 0.698, 0)$, $D(-3.755, -0.698, 0)$, $E(-2.546, -1.397, 0)$, $F(-1.336, -0.698, 0)$, $G(0.672, 0.704, -1.164)$, $H(1.182, 1.366, -2.047)$

Eigenvalue (eV)	Transition Band (mμ)	Important Contributors	Description	Transitions without Ψ_9, Ψ_{10}	exp. [*16*] (n-heptane)
-0.0901		99% Ψ_0	GS		319
3.6045	335	>99% Ψ_6	$n \rightarrow \pi^*$	334	330
4.8138	253	50% Ψ_1, 50% Ψ_4	BLE	252	297
5.6181	217	88% Ψ_3, 9% Ψ_2		217	288
5.9617	204	82% Ψ_2, ~5% Ψ_1, Ψ_3 Ψ_4 each, 1.8% Ψ_7		204	271
7.0197	174	40% Ψ_1, 37% Ψ_4, ~5% Ψ_8, Ψ_2, Ψ_3, Ψ_5 each	BLE + PCCT	173	264
7.7091	158	12% Ψ_7, 84.5% Ψ_8 2.7% Ψ_1, 6% Ψ_4, 5% Ψ_5	PCCT	159	259
7.8427	156	83% Ψ_7, 3% Ψ_2, 13% Ψ_5		156	225
8.4761	144	13% Ψ_7, 8% Ψ_8, 77% Ψ_5	CLE	144	220
8.5926	142	15% Ψ_9, 85% Ψ_{10}	CPCT		197
9.3437	131	85% Ψ_9, 15% Ψ_{10}			182

CPCT = Carbonyl to Phenyl Charge Transfer

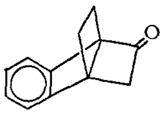
Thus, the formula for calculating these integrals is similar in form to the one used [*22*] in the planar case, only that the coefficients of its "inner parts" have to be separately found beforehand. Bielectronic bicentric integrals related to benzene π-orbitals and oxygen non-bonding electrons are calculated in a similar manner; all monoelectronic α integrals can thus be evaluated.

To calculate the resonance integrals β_{ab}, we use Eq. (4), with the expression

$$S_{ab} = S_{\pi\pi}(A_{ai}A_{bi} + A_{aj}A_{bj}) + S_{\sigma\sigma}(A_{ak}A_{bk})$$

and note two things; first, the overlap between benzene π-orbitals and oxygen non-bonding electrons is not null and β is not zero; interactions between the $n \rightarrow \pi^*$ carbonylic transition and other configurations are discernible even in the ZDO approximation. Secondly, as the overlaps might turn out to be either positive or negative, the doubt concerning the sign of β is again raised. Anyhow, the numerical results of the CI calculation are almost not sensitive to the sign of the few ambiguous integrals.

The results of a calculation, account being taken of the eleven configurations Ψ_0, $\Psi_1 \ldots \Psi_{10}$, are given in Tab. 6 for the structure C, 1,4-dihydro-1,4-ethano-2(3H)-naphthalenone. Also cited are results of a concurrent calculation in which



C

account has not been taken of configurations Ψ_9 and Ψ_{10}; it is seen that such omission is justified: a charge-transfer from carbonyl to phenyl may be of too high energy to influence other transitions.

Considering together the data of Tabs. 4, 5 and 6, we note that the bathochromic shift of the $n \rightarrow \pi^*$ ketonic band, upon interaction with phenyl, is reproduced, though somewhat overestimated. The calculated wavelengths for the various transitions do not differ much from one compound to another; it is rather the nature of the bands and their intensity that depend upon geometry. Together with increased chance of phenyl to carbonyl charge transfer, there is an enlargement of the interaction of this state with other configurations and, in general, in the amount of mixing of the different states: whereas the spectrum of compound A is not much more than a superposition of the contributing parts, there are almost no "pure" configurations in compound C; yet, the placing of the different bands is only slightly affected. Small structural changes suffice to modify the calculated results: most of the bands found for B are more intense than the corresponding bands in A.

Whereas carbonyl to phenyl charge transfers are not of much importance, the reverse transfers react both with ketone and aromatic local excitations, beside their interaction with the $n \rightarrow \pi^*$ transitions. Calculated oscillator strengths serve an additional index, together with the mixing percentages, of the influence of geometry upon the amount of interaction.

One of us (A.Y.M.) is indebted to the "Délégation Nationale à la Recherche Scientifique (Comité Cancer et Leucémie)" for a maintenance grant, and to Prof. B. PULLMAN, for hospitality offered at the Institut de Biologie Physico-Chimique.

References

1. FERGUSON, L. N., and J. C. NNADI: J. chem. Educat. **42**, 529 (1965).
2. KUMLER, W. D., L. A. STRAIT, and E. L. ALPEN: J. Amer. chem. Soc. **72**, 1463 (1950).
3. ALPEN, E. L., W. D. KUMLER, and L. A. STRAIT: J. Amer. chem. Soc. **72**, 4558 (1950).
4. COOKSON, R. C., and N. S. WARIYAR: J. chem. Soc. **1956**, 2302.
5. NAGAKURA, S.: Molecular Physics **3**, 105 (1960) and later papers.
6. MULLIKEN, R. S.: J. Amer. chem. Soc. **74**, 811 (1952).
7. LABHART, H., and G. WAGNIÈRE: Helv. chim. Acta **42**, 2219 (1959).
8. MULLIKEN, R. S.: J. Amer. chem. Soc. **72**, 4493 (1950).
9. MURRELL, J. N.: The theory of the electronic spectra of organic molecules. London: Methuen and Co. New York: John Wiley and Sons 1963.
10. COOKSON, R. C., and J. HUDEC: J. chem. Soc. **1962**, 429.
11. LONGUET-HIGGINS, H. C., and J. N. MURRELL: Proc. Physic. Soc. **68A**, 601 (1955).
12. KIMURA, K., H. TSUBOMURA, and S. NAGAKURA: J. chem. Soc. Japan **37**, 1336 (1964).
13. LAKE, J. S., and A. J. HARRISON: J. chem. Physics **30**, 361 (1959).
14. KASHA, M.: Disc. Faraday Soc. **9**, 14 (1950).
15. TANAKA, J., and S. NAGAKURA: J. chem. Physics **24**, 311 (1956).
16. KITAHONOKI, K., and Y. TAKANO: Tetrahedron Letters **1963**, 1597.
17. COTTON, F. A.: Chemical applications of group theory, p. 128. New York and London: Interscience Publishers 1963.
18. FISCHER-HJALMARS, I.: Adv. Quant. Chem. (Ed. by P. O. LÖWDIN) New York: Academic Press. **2**, 25 (1965).
19. PARR, R. G.: J. chem. Physics **33**, 1184 (1960).
20. LEROY, G.: Bull. Soc. Chim. Belges **75**, 70 (1966).
21. MOFFIT, W.: Proc. Roy. Soc. **210A**, 224 (1951).
22. ROOTHAAN, C. J.: J. chem. Physics **19**, 1445 (1951).

23. Julg, A.: J. Chim. physique **55**, 413 (1958); **56**, 235 (1959).
24. Skinner, H. A., and H. O. Pritchard: Trans. Faraday Soc. **49**, 1254 (1953).
25. Berthier, G., J. Baudet et M. Suard: Tetrahedron **19**, Suppl. 2, 1 (1963).
26. Wolfsberg, M., and L. Helmholtz: J. chem. Physics **20**, 887 (1952).
27. Lykos, P. G.: J. chem. Physics **35**, 1249 (1961).
28. Branscomb, L. M.: Nature **182**, 248 (1958).
29. Pullman, B., and A. Pullman: Quantum biochemistry. London: Interscience Publishers 1963.
30. Data quoted by Pitts, J. N., Jr., and J. K. S. Wan: Photochemistry of ketones and aldehydes, in Patai, S., Ed.: The chemistry of the carbonyl group. New York: John Wiley and Sons 1965.
31. Price, W. C.: J. chem. Physics **3**, 256 (1935).

Dr. A. Y. Meyer
Department of Organic Chemistry
Hebrew University
Jerusalem, Israel