658. *The π-Electronic Structure and Properties of Naphthalene.*

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The " atom " and " bond " populations in naphthalene are calculated. By using different atomic orbital bases the values of the oscillator strengths for the first four singlet excited states are calculated.

VARIOUS authors have recently applied Roothaan's self-consistent field (SCF) method,[1] as modified for π-electron molecules,[2] to a calculation of the structure and properties of naphthalene.[2-5] Pariser [6] published a configuration interaction calculation in which a large number of the singly excited configurations were used. The most satisfactory simplification for the various assumptions involved [2,6] seems to depend on the use of a suitable basis of orthogonalized atomic orbitals, in which case the integrals which are neglected are indeed very small.[7-9] In this paper the SCF bond orders which were calculated on such a basis [4] are transformed into those which occur in the basis of ordinary carbon $2p_z$ atomic orbitals, and are compared with those of an earlier calculation.[10] The values of the oscillator strengths for the first four singlet transitions using the two atomic orbital bases are compared.

Charge Distribution.—The bond orders in the orthogonal atomic orbital basis [11] have been reported previously.[4] These atomic orbitals are neither well localized nor centrosymmetric,[10-12] and therefore the $\bar{P}_{ij}$ which represent the " formal " charges ($i = j$) and bond orders ($i \neq j$) do not give a direct description of the charge distribution in the molecule.

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[1] Roothaan, *Rev. Mod. Phys.*, 1955, **23**, 69.

[2] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[3] Moser and Brion, *J. Chim. phys.*, 1955, **52**, 25; Lefebvre and Moser, *J.*, 1956, 1557, 2743; Pople, *Proc. Phys. Soc.*, 1955, 68, *A*, 81.

[4] Peacock, *Trans. Faraday Soc.*, 1957, **53**, 1042.

[5] Peacock, *Proc. Phys. Soc.*, 1957, **70**, *A*, 654.

[6] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.

[7] McWeeny, *Proc. Roy. Soc.*, 1955, *A*, **227**, 288.

[8] *Idem, ibid.*, 1956, *A*, **237**, 355.

[9] Hall, *Trans. Faraday Soc.*, 1954, **50**, 773.

[10] McWeeny, *J. Chem. Phys.*, 1951, **19**, 1614.

[11] Lowdin, *ibid.*, 1950, **18**, 365.

[12] McWeeny, *Proc. Roy. Soc.*, 1955, *A*, **232**, 114.

If $\mathbf{a}$ is the row matrix $(a_1, a_2, \ldots a_n)$ of $2p$ atomic orbitals and $\bar{a}$ is that of the orthonormalized $2p$ atomic orbitals, then:[11]

$$\bar{\mathbf{a}} = \mathbf{a}\,\mathbf{S}^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where $\mathbf{S}$ is the matrix of overlap integrals.

Let $\overline{\mathbf{T}}$ be an $m \times n$ matrix whose n columns represent the coefficients of the m orthonormal orbitals in the n molecular orbitals.[9] Then $\overline{\mathbf{A}} = (ABC) = \overline{\mathbf{a}\mathbf{T}}$, and the one electron density is

$$P(1) = \sum_{ij} \bar{a}_i(1)\, \overline{P}_{ij}\bar{a}_j{}^*(1)$$

where $\overline{\mathbf{P}} = 2\overline{\mathbf{T}}\overline{\mathbf{T}}^\dagger$ is the density matrix.

If expression (1) is used, alternative expressions are $\mathbf{A} = \mathbf{aT}$ where $\mathbf{T} = \mathbf{S}^{-\frac{1}{2}}\overline{\mathbf{T}}$ and

$$P(1) = \sum_{ij} a_i(1)P_{ij}a_j{}^*(1)$$

where $\mathbf{P} = 2\mathbf{TT}^\dagger = \mathbf{S}^{-\frac{1}{2}}\overline{\mathbf{P}}\mathbf{S}^{-\frac{1}{2}}$. $\mathbf{P}$ is the density matrix in the non-orthogonal basis of ordinary $2p$-orbitals, its elements indicating the charges in well-defined regions.

The amounts of charge assigned to the orbital (atom) and overlap (bond) regions are then (by integration)

$$q_{ii} = P_{ii}$$

and $$q_{ij} = 2P_{ij}S_{ij} \text{ (real orbitals being assumed)}$$

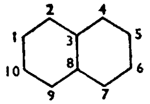
and $$tr\mathbf{PS} = N \text{ (the total number of } \pi\text{-electrons)}$$

These are the orbital and overlap "populations"[13] or "atom" and "bond charges."[10]

Application to Naphthalene.—The numbering used here for naphthalene is given in (I). The values of the overlap integrals are given in Table 1.

TABLE 1.

S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}
0·260	0·039	0·002	0·000	0·000	0·001	0·018



(I)

The matrix $\mathbf{S}^{-\frac{1}{2}}$ was computed by rewriting $\mathbf{S}$ as $(\mathbf{1} + \mathbf{x})$ and expanding as a matrix power series, six terms giving adequate accuracy.

The π-charge distribution in naphthalene is given in Table 2 and compared with that of McWeeny[10] who set all overlap integrals except S_{12} equal to zero. The values of P_{ij} and $\overline{P}_{ij}$ are also given

TABLE 2.

	11	12	22	23	33	38	1,10
q	0·759	0·300	0·772	0·177	0·737	0·211	0·200
q[10]	0·757	0·273	0·767	0·193	0·719	0·178	0·213
P	0·759	0·567	0·772	0·341	0·737	0·405	0·382
$\overline{P}$[4]	1·000	0·754	1·000	0·526	1·000	0·576	0·572

It is seen that each atom has a deficiency of π-electrons and therefore a net positive charge of about 0·2 electron unit while each bond contains a net negative charge of about 0·2.

The Excited States of Naphthalene.—The energies of the excited states predicted by using limited configuration interaction have already been published and discussed.[5] The wave functions for the excited states together with their energies relative to the ground state are given below, B, A, A', and B' being the two highest occupied and two lowest unoccupied orbitals in ascending energy order,

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[13] Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.

TABLE 3.

$$\Psi_p = 0{\cdot}9345\Phi(A \longrightarrow A') + 0{\cdot}3561\Phi(B \longrightarrow B') \qquad E_p = 4{\cdot}54 \text{ ev}$$
$$\Psi_\alpha = 0{\cdot}7071\Phi(A \longrightarrow B') - 0{\cdot}7071\Phi(B \longrightarrow A') \qquad E_\alpha = 4{\cdot}45 \text{ ev}$$
$$\Psi_\beta = 0{\cdot}7071\Phi(A \longrightarrow B') + 0{\cdot}7071\Phi(B \longrightarrow A') \qquad E_\beta = 6{\cdot}34 \text{ ev}$$
$$\Psi_{\beta'} = 0{\cdot}3561\Phi(A \longrightarrow A') - 0{\cdot}9345\Phi(\mathrm{B} \longrightarrow \mathrm{B}') \qquad E_{\beta'} = 6{\cdot}65 \text{ ev}$$

where for example $\Phi(B \longrightarrow B')$ is the wave function of the configuration in which one electron has been excited from molecular orbital B to B'.

The relevant SCF molecular orbitals (in the orthogonal basis) are given in Table 4.

TABLE 4.

$$\psi_B = 0{\cdot}3950\ (\bar{a}_1 + \bar{a}_5 + \bar{a}_6 + \bar{a}_{10}) - 0{\cdot}4336\ (\bar{a}_3 + \bar{a}_8)$$
$$\psi_A = 0{\cdot}2643\ (\bar{a}_1 - \bar{a}_5 + \bar{a}_6 - \bar{a}_{10}) + 0{\cdot}4145\ (\bar{a}_2 - \bar{a}_4 + \bar{a}_7 - \bar{a}_9)$$
$$\psi_{A'} = 0{\cdot}2643\ (\bar{a}_1 - \bar{a}_5 - \bar{a}_6 + \bar{a}_{10}) - 0{\cdot}4145\ (\bar{a}_2 - \bar{a}_4 - \bar{a}_7 + \bar{a}_9)$$
$$\psi_{B'} = 0{\cdot}3950\ (\bar{a}_1 + \bar{a}_5 - \bar{a}_6 - \bar{a}_{10}) - 0{\cdot}4336\ (\bar{a}_3 - \bar{a}_8)$$

The oscillator strength for a transition $\Psi_\alpha \longrightarrow \Psi_\beta$ is given [14] by

$$f_{\alpha\beta} = 1{\cdot}085 \times 10^{11}\,\bar{\nu}Q^2$$

where $\bar{\nu}$ is the frequency of the transition (in wave numbers) and $Q_{\alpha\beta}{}^2$ is given by

$$Q_{\alpha\beta}{}^2 = Q_{(x)\alpha\beta}{}^2 + Q_{(y)\alpha\beta}{}^2 + Q_{(z)\alpha\beta}{}^2$$

where
$$Q_{x(ij)} = e^2\int \Psi_\alpha{}^* \sum^{N} x_i\Psi_\beta \mathrm{d}\tau$$

The contribution to $Q_{x(ij)}$ vanishes except between functions Φ and Φ' which differ in only one orbital, *e.g.*, $A \longrightarrow A'$; the element of Q_x is then given by

$$\sqrt{2}\mathrm{tr}\ \bar{\mathbf{X}}\,\bar{\mathbf{P}}_{AA'}$$

where
$$\bar{\mathbf{P}}_{AA'} = \bar{\mathbf{T}}_A\bar{\mathbf{T}}_{A'}{}^\dagger \text{ and } \bar{X}_{rs} = \int \bar{\phi}_r{}^* x \bar{\phi}_s \mathrm{d}\tau$$

In the non-orthogonal basis

$$Q_X = \sqrt{2}\mathrm{tr}\ \mathbf{X}\,\mathbf{P}_{AA'}$$

where
$$\mathbf{P}_{AA'} = \mathbf{S}^{-\frac{1}{2}}\bar{\mathbf{P}}\mathbf{S}^{-\frac{1}{2}} \text{ and } X_{rs} = \int \phi_r{}^* x \phi_s \mathrm{d}\tau = x_{rs}S_{rs}$$

Since x_{rr} is the centroid of orbital r and x_{rs} that of the centroid of bond rs, and since for ordinary $2p$-orbitals these centroids are at the atom and bond mid-points, the calculation in the non-orthogonal basis is straight-forward. It is customary, however,[6] to make similar assumptions when dealing with the orthogonal orbitals which are implicitly accepted as a basis for the SCF calculations and it is therefore useful to compare this " simplified " treatment with that in which there is a rigorous transformation to the ordinary $2p$-basis. The calculated oscillator strengths for the α, p, β, and β' states are given in Table 5.

TABLE 5.

	α	p	β	β'
Calc. from transition charge density	0	0·208	2·175	1·025
Calc. by assuming (orthonormalized) orbitals and overlap distributions centrosymmetric	0	0·205	2·213	1·040

Table 5 shows that the values of the oscillator strengths obtained by the more convenient orthonormal basis without detailed analysis of the transition charge density are in good agreement with those calculated more rigorously (this inference holds good also in the case

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[14] Mulliken and Rieke, *Reports Progr. Phys.*, 1941, **8**, 231.

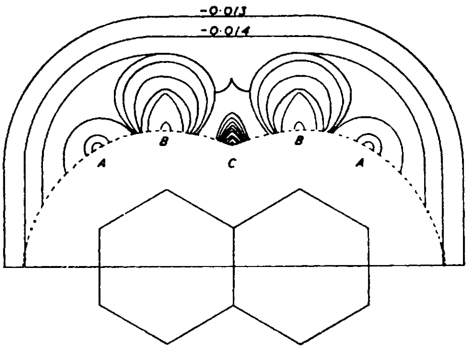
of heteroaromatics[15]). The numerical values given in Table 5 are also in close agreement with those given by Lefebvre and Moser[3] and Pariser.[6]

The Potential Energy outside the Molecule.—The potential energy of a unit-point positive charge moving in the field of the molecule may be represented by

$$V = (\delta_{rs} - q_{rs})/r_{c(rs)} \quad \left(\delta_{rs} \begin{array}{ll} = 1 & r = s \\ = 0 & r \neq s \end{array}\right) \quad . \quad . \quad . \quad . \quad (2)$$

where $r_{c(rs)}$ is the distance between the point charge and the centroid of bond rs (or the atom if $r = s$) and q_{rs} is the orbital ($r = s$) or overlap ($r \neq s$) charge. Here it is assumed, provisionally, that each framework ion may be regarded as a point positive charge. This approximation probably holds at distances far enough away for polarisation effects to be small.

Potential energy contours around the naphthalene molecule (in atomic units).



Numerical values (all negative, except as stated) of successive contours, listed outwards are:
A, 0·023, 0·021, 0·016.
B, 0·010 (positive), 0·004, 0·011, 0·013, 0·014, 0·015.
C, 0·026, 0·022, 0·021, 0·020, 0·019, 0·018, 0·017, 0·016.
At ×, *A* 0·028; *C*, 0·028.

The potential field calculated by using expression (2) has an interesting form (see Figure). The broken circles, of radius 5 atomic units, indicate the closest distance at which expression (2) may be meaningful. Of the points which lie on this circle, those opposite to bonds 1—2 and 2—3 have a potential energy twice as large as the point opposite to bond 1—10.

A cation when it enters the potential field of the molecule will become subject to strong directive influences which will tend to attract it towards the bonds. The actual reaction between ligand and molecule will occur at distances so close that expression (2) will not apply and other effects will be significant. No attempt will be made here to discuss the preferential activity of the α-atoms towards cationic substitution. However, it is interesting that the usual assumptions of uniform distribution in unsaturated hydrocarbons, where there are no net charges, lead to no directing influences on an approaching cation.

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[15] Peacock, unpublished work.