

## ELECTRONIC STRUCTURE OF SOME TETRACYANO-POLYMETHINES

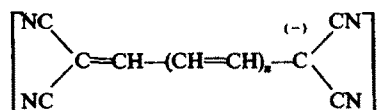
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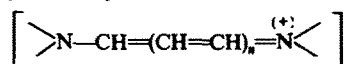
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**Abstract**—PPP and VESCF calculations have been performed on some tetracyano-polymethines. The results for the electronic transition energies and oscillator strengths are compared with experiment. The calculated electronic charge distribution is briefly discussed.

THE electronic structure of some tetracyano-polymethines of the general formula:



have been interpreted.<sup>1</sup> These systems are important since their structure may be taken as a model for the cyanine dyes:



especially with respect to isomerization<sup>2</sup> and aggregation<sup>3</sup> processes, and to the sensitization of silver halide microcrystals.<sup>4</sup>

In the present paper some results of calculations performed on the ground state of tetracyano-polymethines with  $n = 0, 1, 2$  are presented. The *trans-trans* conformation, shown in Fig. 1, was assumed throughout.

The method used is the well-known Pariser Parr and Pople method (PPP)<sup>5</sup> which has been successfully applied to the interpretation of electronic spectra of aromatic molecules, although its applicability has not yet been completely established in the case of heteroaromatic systems. Moreover, in the systems studied here the interest is augmented by the presence of a negative charge. It has been important to consider the choice of parameters to be used in the calculations. Since we were particularly interested in the knowledge of the charge distribution, we also performed calculations using the variable electronegativity method (VESCF).<sup>6</sup> This technique, according to Brown *et al.*,<sup>7</sup> seems to predict a more nearly correct charge distribution representing, in practice, the combined density of  $\pi$  and  $\sigma$  electrons.

Eventually, it is our aim to extend this investigation to the possible isomeric conformers and to the electronic structures of excited states, also of more complicated cyanine dyes with the hope of giving a contribution to the studies of the processes mentioned above.

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*Method of calculations*

The parameters eventually chosen for the PPP calculations were taken as follows:

(a) The valence state ionization potentials (VSIP) of the  $2p_\pi$  orbitals were taken from Hinze and Jaffé<sup>8</sup> and in our case are:

$$W_C = -11.16 \text{ eV (} sp^2 \text{ hybridization)}$$

$$W_C = -11.19 \text{ eV (} sp \text{ hybridization)}$$

$$W_N = -14.18 \text{ eV}$$

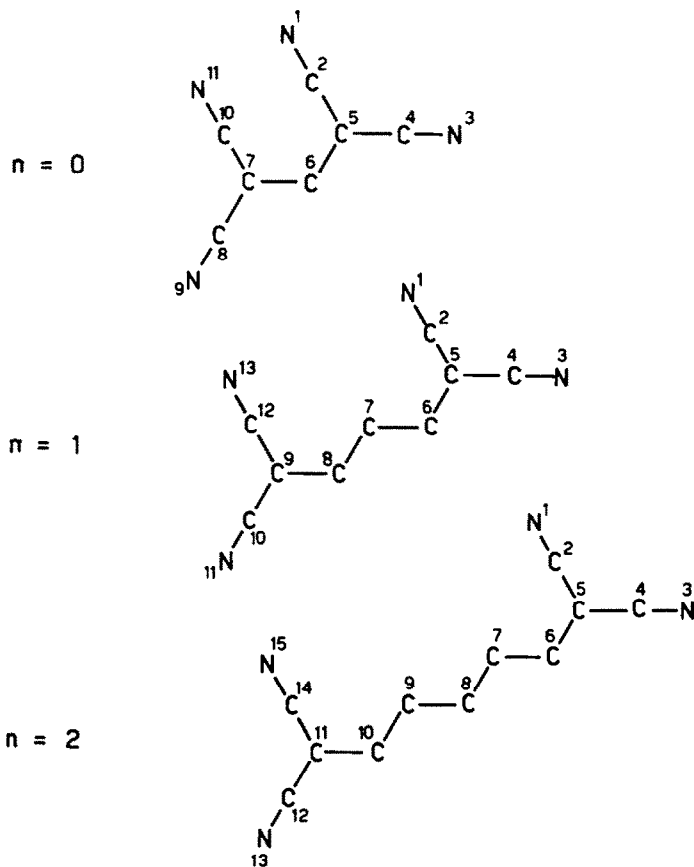


FIG. 1 Skeleton and numbering of the investigated systems. Bond distances C—C = 1.466 Å, C—N = 1.158 Å.

(b) The off-diagonal elements of the core Hamiltonian between the  $p$  and  $q$  neighbouring atoms were calculated using the following relation:

$$\beta_{pq}^{\text{core}} = \frac{1}{2} S_{pq} (W_p + W_q)$$

where  $S_{pq}$  is the overlap integral between the orbitals involved.

(c) The two center Coulomb repulsion integrals were evaluated using the formulae of Nishimoto and Mataga:<sup>9</sup>

$$\gamma_{pq} = 14.397 / (R + a) \text{ where } a = 14.397 / \frac{1}{2} (\gamma_{pp} + \gamma_{qq})$$

and  $\gamma_{pp}$ ,  $\gamma_{qq}$  are the one-centre Coulomb repulsion integrals, taken as the difference between the VSIP and the electron affinity, and  $R$  is the internuclear distance in Å. Penetration integrals were neglected. Configuration interaction was included for singlet-singlet transitions.

In the calculations performed using the VESCF procedure the VSIP's become functions of the effective nuclear charge and were evaluated by a quadratic interpolation along the isoelectronic series. This interpolation was carried out using the  $|\epsilon_{nl}|$  calculated by Clementi<sup>10</sup> which is the Lagrange multiplier of the H.F. scheme corresponding to a valence orbital ( $np_n$ ) of the lowest spectroscopic term in the ground state configurations.\* For the VISP's the following functions are derived:

$$\begin{aligned} -W_C &= 0.30 Z^2 + 10.06 Z - 24.14 \\ -W_N &= -1.27 Z^2 + 25.74 Z - 65.70 \end{aligned}$$

All the calculations were performed on the 7040 IBM Computer of the "Centro di Calcolo" of Rome University.

## RESULTS

In Fig. 2 the spectra of the systems investigated are reported.<sup>1</sup> As it can be seen from

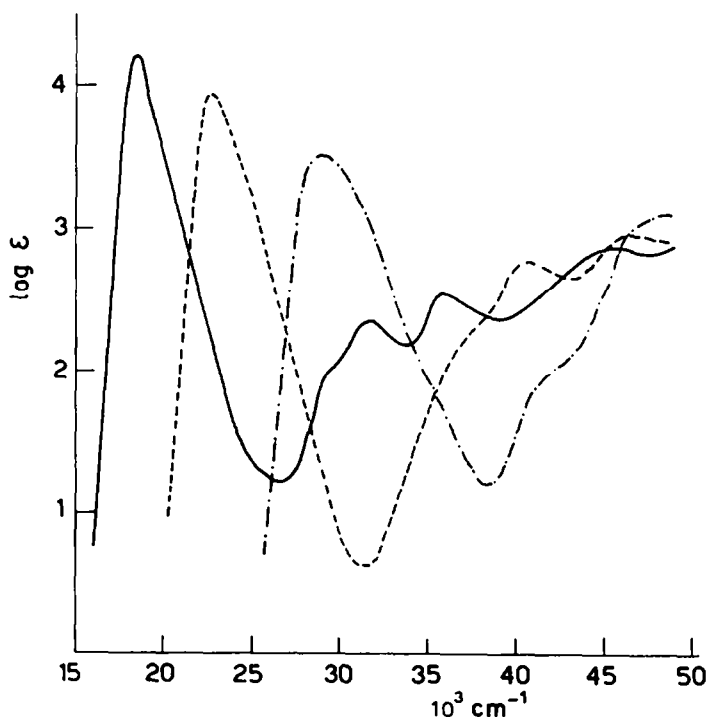


FIG. 2 UV spectra of the tetracyano-polymethines, - · - · - ·  $n = 0$ , - - - - -  $n = 1$ , ———  $n = 2$ .

\* The use of these theoretical values in the PPP calculations does not markedly influence the results.<sup>11</sup>

Table 1, the results of the calculations of electronic transitions obtained with the two methods give satisfactory agreement with experiment. The agreement, as expected, improved with increase of  $n$ . Also, the calculated oscillator strengths give, qualitatively, the correct order of the relative intensities of the longest wavelength bands.

In Table 2 the charge densities and bond orders are reported. The predicted electronic distribution is quite usual, with a decrease of polarity on extending the chromophore. The PPP and VESCF methods, while not differing appreciably in the interpretation of the spectra, do show a certain difference in the charge distribution in the sense that the VESCF method tends to decrease the charge polarities.

TABLE 1. SINGLET-SINGLET TRANSITIONS (IN kK) AND OSCILLATOR STRENGTHS (IN BRACKETS) CALCULATED WITH DIFFERENT APPROXIMATIONS

$n$	PPP	VESCF	exp
0	26.5 (0.79)	24.2 (0.79)	28.9
	37.8 (0.30)	34.4 (0.33)	} 41.3
	38.7 (0.56)	35.3 (0.58)	
1	22.0 (1.39)	20.4 (1.44)	23.1
	37.9 (0.22)	34.6 (0.24)	37.0 (sh)
	38.6 (0.49)	35.2 (0.53)	} 40.4
	42.0 (0.24)	40.6 (0.22)	
2	18.3 (1.88)	17.0 (1.99)	18.5
	35.0 (0.035)	32.7 (0.04)	29.1 (sh)
	36.3 (0.13)	35.2 (0.13)	31.9
	39.4 (0.13)	35.9 (0.14)	35.8
	46.5 (0.029)	45.4 (0.005)	45.2

Other simpler theoretical models, such as the free-electron and Hückel MO methods, have been used with fairly good results in calculations on systems similar to those studied.<sup>2, 12, 13</sup> However, the PPP method, also used successfully for all the bands in the UV spectra, cannot be considered a complicated method, and appears to be more flexible and suitable for an extension of scopes and systems. It is in fact more complete than the Hückel theory from a theoretical point of view and contains a more direct account of the quantum mechanical features than the free-electron model, which should be completed by often uncertain perturbation calculations. Hence the PPP method gives us more confidence for the consideration of some problems that could arise from an extension of our investigation; for instance problems such as *cis-trans* isomers, non symmetrical systems, properties of excited-state configurations and bond alternation, although the latter is not of practical interest in our systems.

It seems, therefore, that the method here used can be applied to a structural study of the cyanine dyes.

TABLE 2. CHARGE DENSITY AND BOND ORDER AS ELEMENTS OF THE  $P$  MATRIX

element	PPP	VESCF	element	PPP	VESCF
$n = 0$					
(1,1)	1.30	1.24	(1,2)	0.88	0.89
(2,2)	0.84	0.92	(3,4)	0.87	0.88
(3,3)	1.32	1.25	(2,5)	0.40	0.41
(4,4)	0.84	0.92	(4,5)	0.42	0.42
(5,5)	1.24	1.18	(5,6)	0.64	0.64
(6,6)	0.92	0.99	(6,7)	0.64	0.64
(7,7)	1.24	1.18	(7,8)	0.42	0.42
(8,8)	0.84	0.92	(7,10)	0.40	0.41
(9,9)	1.32	1.25	(8,9)	0.87	0.88
(10,10)	0.84	0.92	(10,11)	0.88	0.89
(11,11)	1.30	1.24			
$n = 1$					
(1,1)	1.29	1.23	(1,2)	0.89	0.89
(2,2)	0.84	0.91	(3,4)	0.88	0.89
(3,3)	1.31	1.24	(2,5)	0.39	0.40
(4,4)	0.84	0.91	(4,5)	0.40	0.40
(5,5)	1.21	1.16	(5,6)	0.66	0.66
(6,6)	0.93	0.99	(6,7)	0.63	0.63
(7,7)	1.16	1.12	(7,8)	0.63	0.63
(8,8)	0.93	0.99	(8,9)	0.66	0.66
(9,9)	1.21	1.16	(9,10)	0.40	0.40
(10,10)	0.84	0.91	(9,12)	0.39	0.40
(11,11)	1.31	1.24	(10,11)	0.88	0.89
(12,12)	0.84	0.91	(12,13)	0.89	0.89
(13,13)	1.29	1.23			
$n = 2$					
(1,1)	1.28	1.22	(1,2)	0.89	0.90
(2,2)	0.84	0.91	(3,4)	0.89	0.90
(3,3)	1.29	1.23	(2,5)	0.39	0.40
(4,4)	0.84	0.91	(4,5)	0.39	0.39
(5,5)	1.20	1.14	(5,6)	0.67	0.68
(6,6)	0.93	0.99	(6,7)	0.61	0.61
(7,7)	1.15	1.11	(7,8)	0.64	0.64
(8,8)	0.94	0.99	(8,9)	0.64	0.64
(9,9)	1.15	1.11	(9,10)	0.61	0.61
(10,10)	0.93	0.99	(10,11)	0.67	0.68
(11,11)	1.20	1.14	(11,12)	0.39	0.39
(12,12)	0.84	0.91	(11,14)	0.39	0.39
(13,13)	1.29	1.23	(12,13)	0.89	0.90
(14,14)	0.84	0.91	(14,15)	0.89	0.90
(15,15)	1.28	1.22			

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