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Relationes

Application of the Pariser-Parr-Pople Method to the Croconate Ion ($C_5O_5^{-2}$)

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Introduction

The electronic structure of hetero-aromatic molecules is commonly studied by the semi-empirical SCF–LCAO–MO theory with or without configuration interaction and the predicted energies of the first excited levels are generally in fair agreement with the observed spectra.

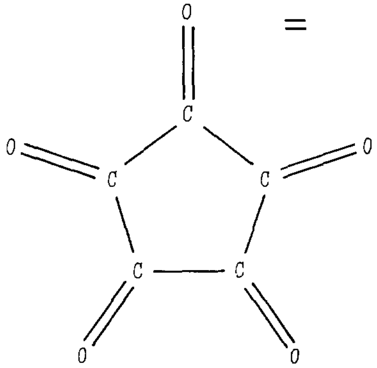

Fig. 1. Croconate ion

The use of the semi-empirical SCF–MO theory of Pariser-Parr-Pople (P–P–P) [1] to investigate the π-electron structure of the croconate ion (Fig. 1) emphasizes a critical choice of the approximations for the parameters or the possibly non-generalizable application of the method, in its present form, to the evaluation of transition energies [2]. These are the justifications required by NISHIMOTO and FORSTER [3] in order to add a new note to the already voluminous literature describing the results of P–P–P treatments.

Calculations

The croconate ion (Fig. 1) is a planar system (D_{5h}) of 10 centers and 12 π-electrons, whose mean C–C (1.457 Å) and C–O (1.262 Å) distances have been determined by an X-ray study on the crystal of the diammonium salt [4].

Two alternative valence states have been considered here for oxygen: O ($tr^2\,tr^2\,tr\,\pi$) or O (sp^2) and O ($s^2\,p^2\,p\,p$) or O (nonhyb); carbon was taken as trigonal C (sp^2). Their ionization potentials are [5]: W [O (sp^2)] = -17.70 eV, W [O (nonhyb)] = -17.28 eV, W [C (sp^2)] = -11.16 eV.

The core resonance integrals β_{pq} have been approximated, except in one case (see Tab. 1), with the formula [6]

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

The inter-π-electronic repulsion integrals γ_{pq} have been calculated either theoretically (T integrals) [7] with a parabolic interpolation for $r < 2.80$ Å or with the procedure described by NISHIMOTO and MATAGA (NM integrals) [12]; the following one-center repulsion integrals γ_{pp} were used [8]: $\gamma_{\mathrm{CC}} = 10.69$ eV and $\gamma_{\mathrm{OO}} = 15.38$ eV.

Penetration integrals ($A\!:\!\pi\pi$) have been approximated by representing the potential due to the neutral atom as a combination of nuclear attraction and electronic repulsion terms over hybrid or pure orbitals [9]. In this way the chosen oxygen valence state influences the numerical value of ($A\!:\!\pi\pi$) (see Tab. 1).

Table 1. *Penetration Integrals* (eV)

integral	distance	O (sp^2)	O (nonhyb)
(O:CC)	1.262	−2.898	−0.978
(O:CC)	2.42	−0.675	−0.090
(O:OO)	2.93	−0.274	−0.053
(C:CC)	1.457	−0.829	
(C:CC)	2.34	−0.028	
(C:OO)	1.262	−1.660	
(C:OO)	2.42	−0.012	

Results and Discussion

The results obtained in the various alternatives are presented in Tab. 2 where V_1 and T_1 are the diagonal elements, referring to the lowest degenerate singlets and triplets of the corresponding C.I. matrices.

The critical choice in the parameters' approximation is evident from the calculated T_1 values which show that the ground state is randomly predicted as a singlet or as a triplet.

Plotting T_1 versus $\delta\alpha = \alpha_{\mathrm{O}} - \alpha_{\mathrm{C}}$ (Fig. 2) for the cases in which the γ_{pq} are approximated with the same criteria (the small difference in the β_{CO} for [O sp^2] and O [nonhyb] can be disregarded) we obtain a linear correlation between T_1 and $\delta\alpha$; it is this difference and not the actual value of the α's which determines the T_1 values. We have to recall at this point that the numerical value of the one-center core integrals depends not only on the γ_{pq} and ($A\!:\!\pi\pi$) but on the so called $W_{2p\pi}$ approximation [10] and this might be the crucial point for the present case. Retaining the validity of the $W_{2p\pi}$ approximation it is possible to state that the T_1 energy calculated with the γ_{pq} (NM) is always lower [3, 11] than that calculated with the γ_{pq} (T).

Table 2

alternatives[a]	energies (eV)[b] of		one-center one-electron integrals (eV)			charge densities		bond orders	
	V_1^c	T_1	α_C	α_O	$\delta\alpha = \alpha_O - \alpha_C$	q_C	q_O	p_{CC}	p_{CO}
a	3.20	0.45	−65.11	−61.39	+3.72	.770	1.630	.649	.393
b	2.83	−0.49	−71.07	−63.62	+7.45	.980	1.420	.732	.380
c	3.15	0.35	−65.11	−60.97	+4.14	.788	1.612	.758	.394
d	3.02	0.06	−67.98	−62.75	+5.23	.847	1.553	.686	.392
e	3.10	0.22	−61.40	−56.69	+4.71	.817	1.583	.672	.392
d′	2.69	−0.15	−67.80	−62.70	+5.10	.816	1.584	.682	.380
f	2.86	0.09	−49.66	−50.62	−0.96	.861	1.539	.686	.400
g	2.63	−0.72	−55.62	−52.85	+2.57	1.060	1.340	.738	.386
h	2.82	−0.01	−49.66	−50.20	−0.54	.880	1.520	.692	.402
l	2.73	−0.26	−52.53	−51.98	+0.55	.937	1.463	.710	.400
i	2.77	−0.14	−45.95	−45.92	+0.03	.910	1.490	.702	.400

[a] Description of different alternatives

a) O (sp^2) ; γ_{pq} (T) ; no ($A{:}\pi\pi$) ; $\beta_{CO} = -2.85$ eV; $\beta_{CC} = -2.49$ eV
b) O (sp^2) ; γ_{pq} (T) ; with ($A{:}\pi\pi$); −2.85 eV; −2.49 eV
c) O (nonhyb); γ_{pq} (T) ; no ($A{:}\pi\pi$) ; −2.80 eV; −2.49 eV
d) O (nonhyb); γ_{pq} (T) ; with ($A{:}\pi\pi$); −2.80 eV; −2.49 eV
d′) O (nonhyb); γ_{pq} (T) ; with ($A{:}\pi\pi$); −2.18 eV; −1.83 eV [*15*]
e) following Bratoz and Besnaionou [*17*] the α's have been evaluated using:
$U_p = W_p - \sum_{p \neq q} (A_q{:}\pi\pi)$; $U_C = -7.45$ and $U_O = -13.00$; γ_{pp} (T); $\beta_{CO} = -2.80$ eV; $\beta_{CC} = -2.49$ eV
f) O (sp^2) ; γ_{pp} (NM); no ($A{:}\pi\pi$) ; $\beta_{CO} = -2.85$ eV; $\beta_{CC} = -2.49$ eV
g) O (sp^2) ; γ_{pq} (NM); with ($A{:}\pi\pi$); −2.85 eV; −2.49 eV
h) O (nonhyb); γ_{pq} (NM); no ($A{:}\pi\pi$) ; −2.80 eV; −2.49 eV
i) O (nonhyb); γ_{pq} (NM); with ($A{:}\pi\pi$); −2.80 eV; −2.49 eV
l) as in (e) ; γ_{pq} (NM) ; −2.80 eV; −2.49 eV

[b] Referred to the ground state energy (0.0 eV).

[c] The first experimental transition is ~3.40 eV.

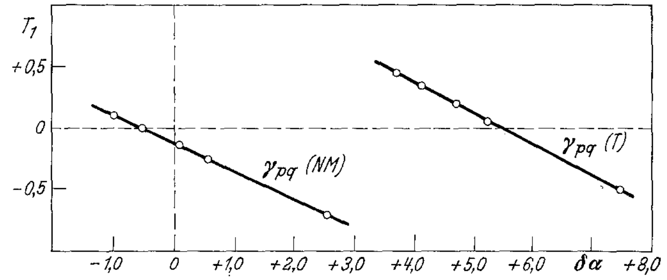

Fig. 2. Calculated triplet energies versus $\delta\alpha = \alpha_O - \alpha_C$

We have not carried out a C.I. treatment since this would give a lower value of T_1 in contrast to the diamagnetism of the croconate ion [*13*]*.

Concerning the role of the core resonance integrals β_{pq} we have tentatively used (see Tab. 2, case d′) the approximation suggested by Kon [*15*] which gives

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* Calculations of P-P-P type on the $C_6O_6^{-2}$ ion [γ_{pq} (T), no ($A{:}\pi\pi$)] also predict a negative value of T_1. Simple LCAO–MO calculations [*14*] predict a biradical nature for $C_6O_6^{-4}$. However $K_4C_6O_6$ was observed to be diamagnetic.

$\beta_{CC} = -1.83$ and $\beta_{CO} = -2.18$ eV. Also in this case T_1 comes out negative. An empirical choice of the β's seems to be outside the scope of a general application of the P–P–P method.

The charge distributions and the bond orders are very sensitive to the inclusion of penetration integrals and the figures of Tab. 2 can be compared with those obtained [*4*] with the simple Hückel MO treatment.

It is possible that the results of our P–P–P calculations depend critically on the assumed D_{5h} symmetry of the $C_5O_5^{-2}$ ion. A similar occurrence was pointed out before by Liehr [*18*] for the C_5H_5 radical, which has its most stable state of C_{2v} or C_s symmetry. It is indeed possible that the geometry of $C_5O_5^{-2}$ established on crystals by X-ray diffraction [*4*], IR and Raman spectra [*19*] might not be appropriate for the ion in solution.

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