Inorganica Chimica Acta, 29 (1978) L253–L255
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Charge Densities and Electronic Transitions in 1-(3-Pyridyl)-1,3-butanedione Anion

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Received May 11, 1978

Introduction

Recently, the magnetic and spectral properties of divalent metal complexes of 1-(3-pyridyl)-1,3-butanedione, $M(pbd)_2$, and 4,4,4-trifluoro-1-(3-pyridyl)-1,3-butanedione, $M(tfpbd)_2$, have been reported [1]. The studies revealed that the structures of these chelates are slightly different from those of the corresponding acetylacetonates, $M(acac)_2$. Infrared spectra [2, 3] and normal coordinate analysis [4] appear to strengthen this observation.

Molecular orbital calculations have been applied to the electronic structure of acetylacetonates as an aid in the interpretation of the spectra of the π-electron systems [5–8]. The results have shown that the charge density distribution on the acetylacetonate anion is generally symmetrical. However, the magnitudes of the charge densities and energies depend largely on the choice of parameters [8].

As a further check on the effect of pyridyl ring substitution in acetylacetonate the Huckel molecular orbital calculations, modified by the ω-technique, have been carried out on nicotinylacetonate (pbd) anion. The charge densities and electronic transition frequencies were evaluated and discussed.

Calculations

In the Huckel theory, the normalized molecular orbitals Ψ written as a linear combination of atomic orbitals Φ (the LCAO approximation) takes the form:

$$\Psi_j = \sum_j C_{ij}\Phi_j \qquad (1)$$

where j extends over all the atoms in the π-electron system and the Ψ's are assumed to be solutions of equation

$$H\Psi = E\Psi \qquad (2)$$

Here, H is a one electron operator and E the energy. The coefficients C_{ij} are derivable from the secular equation

$$\Sigma\, C_{ij} \int \phi_j\,(H - E)\,\Phi_k d\tau = 0 \qquad (3)$$

Defining, in the usual manner, the coulomb (α), resonance (β) and overlap (S) integrals as

$$\begin{aligned} \alpha_j &= \int \Phi_j H \Phi_j d\tau \\ \beta_{jk} &= \int \Phi_j H \Phi_k d\tau \qquad (4) \\ S_{jk} &= \int \Phi_j \Phi_k d\tau \end{aligned}$$

the final equation becomes

$$\Sigma\, C_{ij}\,(H_{jk} - ES_{jk}) = 0 \qquad (5)$$

where $H_{jk} = \alpha_j$ if $j = k$
$= \beta_{jk}$ if $j \neq k$

This equation has a non-trivial solution when

$$|H_{jk} - ES_{jk}| = 0 \qquad (6)$$

The essential features of Huckel theory are that $\beta_{jk} = 0$ for non-bonded atoms j and k and $S_{jk} = 0$ for $j \neq k$ and one for $j = k$ provided the Φ's are normalized. There are several modifications to this theory. The one employed in this calculation is the ω-technique introduced by Streitiviesser [9, 10]. By this, the coulomb integral α is corrected for the situation in which the charge density $q \neq 1$ in the π-lattice system. Thus

$$\alpha_k = \alpha_o + (1 - q_k)\,\omega\beta_o \qquad (7)$$

where co is a dimensionless parameter taken as 1.4 [9]. For nuclei contributing two electrons to the π-system

$$\alpha_k = \alpha_o + (2 - q_k)\,\omega\beta_o \qquad (8)$$

The resonance integrals β are modified by the bond length relationship to

$$\beta_{jk} = \beta_o \exp[-(r_{jk} - 1.397)/0.3106] \qquad (9)$$

where r_{jk} is the bond length between atoms j and k [9–12].

The computation was carried out on an IBM 370/135 computer using the computer program QCPE 110 from Quantum Chemistry Program Exchange.

The initial input parameters of coulomb and resonance integrals are given in Table I. These were refined by an iterative method until a self-consistent energy was obtained.

Results and Discussion

The calculated electronic transition frequencies are compared with the observed values in Table II. In acetylacetonate anion, three filled molecular orbitals are expected with a transition to the first

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TABLE I. Coulomb (α) and Resonances (β) Integrals for Nicotinylacetonate Anion in Units of β (β = 22,000 cm^{-1}).

Parameters	Initial Values	
	Roberts [12]	Electronegativity Difference [9]
α_C	0.00	0.00
α_O	1.60	1.00
α_N	1.00	0.50
β_{CC}	1.00	1.00
β_{CO}	0.76	0.76
β_{CN}	0.84	0.84
β_{CPY}	0.78	0.78
$\beta_{CC'}$[a]	0.93	0.93

[a] The prime refers to the carbon atom close to an oxygen atom.

empty orbital designated by $\pi_4^* \leftarrow \pi_3$ [8]. In pbd anion with six filled molecular orbitals, the corresponding transition has been attributed to $\pi_7^* \leftarrow \pi_6$. The assignments of these transitions in the nicotinylacetonate anion are included in Table II. The results obtained, using Roberts parameters [13] (Method I in Table II), seem to give a better agreement with the observed values than the parameters derived from electronegativity difference [9] (Method II in Table II). Modification of the integrals by the ω-technique was found to have improved the results especially when the ionic charge is away from the pyridyl ring (Method IA). This would probably indicate that the ionic charge is unlikely to be localized on the oxygen atom close to the pyridyl ring.

Bands I and III are the most sensitive to the parameter choice while Band II appears to be unaffected. This seems to reinforce our earlier interpretation that Bands I and III are largely influenced by the metal ions and therefore originate from the β-diketonate ring [1]. On the other hand, Band II could be associated with the transition within the pyridyl ring generally observed in free pyridine at *ca.* 38,000 cm^{-1} [1, 14]. The fourth transition (Band IV) is attributed to an inner orbital transition which occurs beyond the limit of our instrument, hence not observed in the reflectance spectra [1]. The assignment of this band is, however, consistent with the corresponding one in acetylacetonates [8].

The calculated charge densities are shown in Figs. 1 and 2. In comparison with the acetylacetonate anion, the charge density on the central carbon atom (*i.e.* position 3) is considerably reduced in the pbd anion. Further, the charge density distributions are

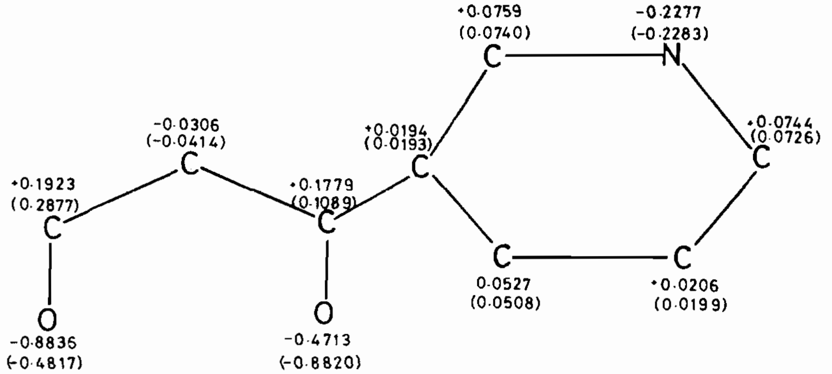

Figure 1. Charge density distributions for 1-(3-pyridyl)-1,3-butanedione anion using Roberts parameters. For values in parenthesis, the ionic charge is close to the pyridyl ring.

TABLE II. Calculated and Observed Electronic Transitions (cm^{-1}) for Nicotinylacetonate Anion.[a,b]

	Method I			Method II			Observed	Assignment
	HMO	ω-Technique		HMO	ω-Technique			
		A	B		A	B		
Band I	31,500	29,600	23,700	24,800	23,600	18,300	28,000	$\pi_7^* \leftarrow \pi_6$
Band II	38,200	37,700	36,000	37,700	40,200	37,400	37,800	Py $\pi \leftarrow \pi$
Band III	48,500	45,700	43,100	41,300	44,900	41,900	45,200	$\pi_9^* \leftarrow \pi_6$
Band IV	56,580	55,400	53,620	45,640	52,610	51,400	–	$\pi_7^* \leftarrow \pi_5$

[a] For the ω-technique, ionic charge was placed on the oxygen atom away from (A) or close to (B) the pyridyl ring. [b] HMO is simple Huckel Molecular Orbital without modification.

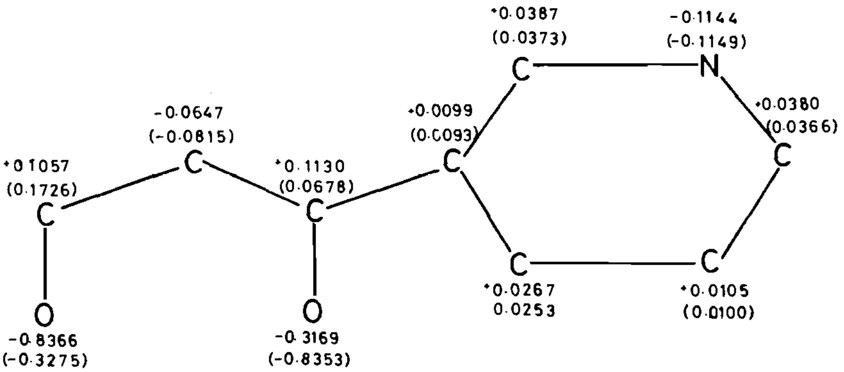

Figure 2. Charge density distributions for 1-(3-pyridyl)-1,3-butanedione anion using electronegativity difference. For values in parenthesis, the ionic charge is close to the pyridyl ring.

not symmetrycal as was the case in acac anion [8]. These can be interpreted in terms of deactivation of the chelate ring by the presence of the pyridyl ring system. The overall net effect is thus to render the 3-position less reactive towards electrophilic substituents.

Acknowledgement

The financial assistance of a University of Ibadan Senate Research Grant is gratefully acknowledged.

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