SOME ASPECTS OF STRUCTURE AND BONDING IN THE PERCHLORODIPHENYLAMINYL RADICAL REVEALED BY ESCA

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Abstract—The ESCA core level spectra of the perchlorodiphenylaminyl radical have been measured and are interpreted in terms of a significant unpaired spin density on nitrogen. Comparison is drawn with conclusions based on the corresponding ESR data. Satellites are observed to the low kinetic energy side of the direct photoionization peaks and these are interpreted in terms of $\pi \rightarrow \pi^*$ shake up transitions accompany core ionizations.

There has been considerable interest on both an experimental and theoretical front in the investigation of multiplet effects accompanying core ionization with the predominant emphasis to date being on paramagnetic transition metal complexes.[1] With the present background of available information the investigation of multiplet effects in the core ionization of transition metal complexes provides a useful tool for the investigation of spin state, stereochemistry, oxidation state and distribution of unpaired electrons which is becoming of increasing importance.[1]

By contrast there have been relatively few investigations of paramagnetic organic systems; the published data being confined to the diphenyl picryl hydrazyl[2] radical and ditertiary butyl and ditrifluoromethyl nitroxide systems.[3] Although in principle ESCA studies of multiplet effects in such systems should (and in the case of the nitroxides does) provide a means of investigating unpaired spin distributions there are relatively few stable organic free radicals which may conveniently be studies with conventional instrumentation. From available theoretical calculations it is clear that even for systems in which an unpaired electron is essentially localized on an atom (e.g. C, N or O) the multiplet splitting in the 1s core levels is predicted to be quite small (1–2 eV), comparable to the typical instrumental resolution.[1a–1c] Indeed for the two systems which has been studied in most detail the multiplet splittings in each were manifest as broadening of the core level signals since there is considerable delocalization of the unpaired electron in both cases.[3]

In recent years a new class of stable organic free radicals have been produced by synthetic routes pioneered by Ballester et al.[4] The basic rationale behind the work is to sterically shield the site of high spin density by appropriate chlorine substitution. In this way for example the perchlorodiphenylaminyl radical has been prepared[4] as a stable solid which may be kept in air on a time scale of months without appreciable oxidation. ESR studies at first sight suggest a high degree of spin localization on nitrogen comparable with diphenyl picryl hydrazyl and somewhat less than for ditertiaryl butyl nitroxide, however the magnitude of the hyperfine splitting as a measure of spin localization is ambiguous since distortion from planarity about the nitrogen can lead to substantial s character for the singly occupied molecular orbital the net effect being that quite a small spin density

could lead to an appreciable hyperfine coupling.[5] The relative chemical inertness of the perchlorodiphenylaminyl radical could therefore possibly arise from extensive delocalization of spin density over the phenyl substituents with a relatively small spin density on nitrogen which constitutes the reactive centre. Steric hindrance provided by the four ortho chlorines could then explain the relative inertness of the system. The substantial hyperfine splitting on nitrogen in this case would be explicable in terms of significant 2s character on nitrogen for the singly occupied MO.[5a–d] This is not unreasonable on the basis of molecular models which indicate considerable distortion about the CNC centre. The alternative rationalization of the available data would be that the unpaired electron is essentially localized on nitrogen, the chemical inertness again being attributable to the steric hindrance to approach provided by the four ortho chlorines. The magnitude of the hyperfine splitting however would suggest that if this were the case the singly occupied molecular orbital must have a large amount of nitrogen 2 p character so that the splitting arises from indirect polarization.

To investigate these alternative possibilities we report here a study of the core level spectra of the perchlorodiphenyl aminyl radical which goes some way to presenting a consistent overall picture of the electronic structures of the system.

RESULTS AND DISCUSSION

The core level spectra (N_{1s}, C_{1s}, Cl_{2s}, Cl_{2p}) for the perchlorodiphenylaminyl radical are shown in Fig. 1 and the derived data are tabulated in Table 1. Considering firstly the C_{1s} spectrum this consists of a single peak centred at ~ 286.7 eV somewhat lower in binding energy

Table 1.

Core level	FWHM (in eV)	Binding energies (eV)	Shake up satellites energy (eV)	% of direct photoionization peak
N_{1s}	1.1	401.4(1)	5.4	4.3
	1.1	400.8(3)		
C_{1s}	1.2	286.7	4.5	2
			5.6	6
			10.4	3
Cl_{2s}	2.1	271.8		
$Cl_{2p1/2}$	1.2	202.5	5.7	1.6†
$Cl_{2p3/2}$	1.2	201.0	5.7	1.6†

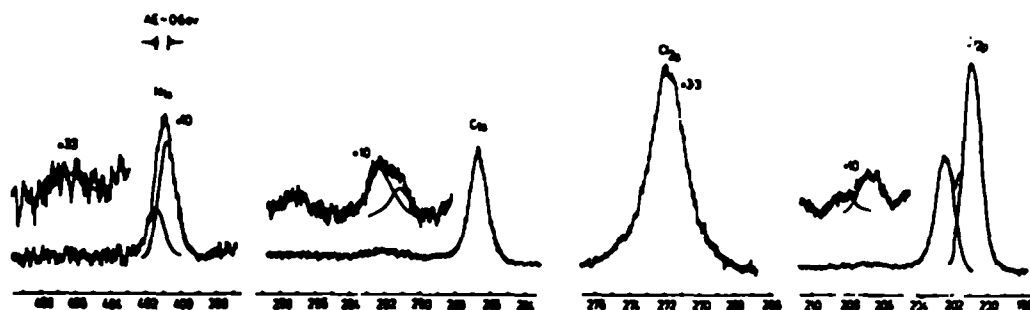†Expressed as percentages of corresponding spin orbit split components.

Fig. 1. Core level spectra for the perchlorodiphenylaminyl radical.

than the chlorine substituted carbons in pentachlorobenzene (287.5 eV).[6] This is not entirely unexpected on the basis of the electronic effect associated with replacing hydrogen by a nitrogen functional group. The carbons directly attached to nitrogen are sufficiently perturbed by the chlorine substituents in the ring system to be considerably shifted to higher binding energy (ÇH in pentachlorobenzene 286.2 eV) such that fortuituously their binding energies are essentially the same as that appropriate to the Ç–Cl structural features.[6] The net effect therefore is that the overall line shape and line width for the direct photoionization peak for the C_{1s} levels is essentially that appropriate to a single component (FWHM 1.2 eV). Before discussing the satellites to the low kinetic energy side of the direct photoionization peaks (attributable to $\pi \rightarrow \pi^*$ shake up satellites) we may briefly consider the measured binding energies and FWHM for the other core levels. The nitrogen core level spectrum shows a somewhat asymmetric line shape suggesting that it arises from the superposition of two components. Analysis of the line shape in terms of two components of intensity ratio 1:3 may straightforwardly be accomplished and the derived energy separation of 0.6 eV is comparable with that measured for the N_{1s} levels of the nitroxides but substantially smaller than for NO (1.4 eV) or NF_2 (1.9 eV) for which there is a large degree of spin localization on nitrogen. The ESCA data show however that there must be a significant unpaired spin density on nitrogen and the ESR data therefore imply a very small degree of nitrogen 2s character. The binding energy of the N_{1s} levels is closely similar to that for perchloroindolenin which forms a suitable model for comparison

purposes.[7] The Cl_{2s} and $Cl_{2p3/2}$ core levels having binding energies which again are consistent with pentachlorophenyl residues linked by nitrogen, being somewhat lower than for pentachlorobenzene.

The evidence from the direct photoionization of the core levels therefore would seem to support an interpretation of the ESR spectra in terms of considerable localization of the unpaired electron although this does not necessarily preclude the possibility of there being a very small contribution from the nitrogen 2s orbital.

It is also of interest to note that for the dimethyl aminyl radical the hyperfine coupling constant is somewhat larger (14.8 gauss)[5d] which is also indicative of more extensive delocalization in the perchloro diphenyl aminyl system.†

For the N_{1s} hole state the multiplet splitting is given as $\Delta E = f \times K$ where f is the fraction of unpaired spin density on nitrogen and K is the one center exchange integral between a core and valence electron on nitrogen.[1c] In the spirit of the transition formalism[8] it is clear that the unpaired spin density appropriate to this relationship is that for the half ionized species and as such the spin density is somewhat modified with respect to the ground state. Thus for a simple system such as NO the calculated (INDO) unpaired spin densities at the nitrogen and oxygen for the ground state are 15% and 28% larger respectively that those appropriate to the half ionized systems (computed from the equivalent cores species).[8] Unfortunately the perchlorodiphenyl aminyl radical is inconveniently large for calculations at the INDO level to be straightforwardly available. As a prototype system to investigate the likely relationship between spin density in the ground state as opposed to the half ionized transition state therefore calculations have been carried out on conformers of the parent diphenylaminyl radical and the N_{1s} core hole state species simulated by the appropriate equivalent cores species. For a

†It should be noted that the linewidth observed for the perchloro diphenyl aminyl is quite large (4 gauss) which may be attributed to unresolved hyperfine splitting involving the chlorines.

bond angle about nitrogen of 103.4° and standard bond lengths[9] the unpaired spin density on nitrogen for the neutral system is somewhat dependent on the relative conformation of the two phenyl groups. Thus with the plane of the rings at an angle of 45° with respect to the plane through the nitrogen and attached two carbon atoms the unpaired spin density on nitrogen is some 5% lower for the equivalent core species. With one of the phenyl groups in plane and the other rotated by 90° the change in unpaired spin density in going from the ground state to the half ionized species is even less ~2%. It should be clear from this that the spin densities appropriate to the interpretation of multiplet effect in ESCA and in hyperfine splittings in ESR are subtly different. For the former the spin distribution is that appropriate for a half ionized system as is clear from the transition formalism, whilst for the latter the spin distribution is that appropriate to the neutral system. Model calculations would seem to provide strong evidence that the spin densities are not significantly different for the two situations, however the tendency will undoubtedly be in a sense that the apparent spin density on nitrogen in the diphenyl aminyl system will be slightly smaller as adjudged by data pertaining to the half ionized state. Since the exchange integral K does not depend strongly on the extent of s and p mixing, multiplet splitting should therefore reflect fairly directly the unpaired spin density at nitrogen. This contrasts strongly with the situation for the ESR spectra where the hyperfine coupling is a sensitive function of the s contribution to the singly occupied molecular orbital. In this respect therefore the unpaired spin density on nitrogen can more readily be investigated by ESCA and the multiplet splitting for the N_{1s} core levels would seem to indicate quite clearly that the unpaired spin density on nitrogen in the perchloro diphenyl aminyl radical is quite substantial.

The core level spectra displayed in Fig. 1 show evidence of satellites to the low kinetic energy side of the direct photoionization peaks. Such satellites have been well documented for unsaturated systems and originate in $\pi \rightarrow \pi^*$ shake up transition accompanying core ionization.[10] For the C_{1s} levels shake up transitions centred ~4.5, 5.6 and 10.4 eV from the direct photoionization peak are observed with relative intensity 3, 6 and 2% with respect to the direct photoionization peak. For the Cl_{2p} and N_{1s} levels satellites are also observed at energy separations of ~5.7 eV and ~5.4 eV respectively, the satellites for the Cl_{2p} levels exhibiting the characteristic spin orbit coupling (1.5 eV) of the direct photoionization peak. The shake up intensities for the N_{1s} and C_{1s} levels are significantly higher than for the Cl_{2p} levels indicative of the fact that the transitions involve occupied and virtual orbitals with small contributions from Cl_{2p} valence orbitals. Although strictly speaking there is no sigma pi separability it is nonetheless convenient to discuss the shake up transitions in terms of the local symmetry of the pi system of the component building blocks for the perchloro diphenyl aminyl system. In previous papers we have studied in some detail the low energy shake up satellites of substituted aromatic ring systems and shown that the low energy satellites in the region <8 eV from the direct photoionization peaks originate in transitions involving the two highest occupied and lowest unoccupied molecular orbitals of the pi systems.[10] The situation with regard to systems with unpaired valence electrons is considerably more complex

since transitions involving both the singly and doubly occupied oribitals are of some importance. The striking feature clearly evident in comparing the shake up structure for the C_{1s} levels of the perchloro diphenyl aminyl system with that for simple substituted phenyl derivatives however is the significantly higher intensity of the low energy shake up structure and the greatly reduced transition energies. The shake up intensity for both the N_{1s} and Cl_{2p} levels is considerably lower and the centroid of the peaks correspond in energy to the higher energy of the two low energy satellites for the C_{1s} levels. By analogy with the substituted aromatic systems which has been studied[10,11] the low energy satellites almost certainly originate in transitions involving the two highest occupied and low unoccupied M.O.'s. In the particular case of the C_{1s} levels where the region to the low kinetic energy side of the direct photoionization peak has been studied in somewhat more detail an additional higher energy (10.4 eV) transition is also apparent. It is interesting to note that the lowest energy component of the shake up transitions for the C_{1s} levels corresponds quite closely in energy to the most intense of the UV-visible transitions for the radical (λ_{max} 296 mμ, 4.2 eV).

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