Photoelectron Spectroscopy of Carbonyls. 1,4-Benzoquinones[1]

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Abstract: He I photoelectron spectra have been obtained for 1,4-benzoquinone (PBQ) and some selected derivatives. A correlative study, which is based on the vibronic characteristics of the various ionization events and on the differential sensitivities of these events to chemical substitution (usually methylation, fluorination, or chlorination) on the benzenoid ring, leads to an MO assignment for the low-energy ionization regime. The assignment for PBQ, in order of decreasing MO energy, is $n_- > n_+ > \pi_\oplus > \pi_-$; that for tetrafluoro-1,4-benzoquinone (TFPBQ) is $n_+ > n_- > \pi_- > \pi_\oplus$. The perfluoro effect on PBQ induces shifts of the n orbitals which are ~1 eV. The perfluoro shifts of the π orbitals are somewhat smaller than those of the n orbitals. CNDO/2 computations provide uniformly poor agreement with the experimental data and retain no assignment utility unless used in a perturbative sense.

The topmost, filled molecular orbitals (MO's) of 1,4-benzoquinone (*p*-benzoquinone or PBQ) consist of two "lone pair" n MO's and two "delocalized" π MO's. These four MO's, as calculated using the CNDO/2 algorithm,[2] are shown in Figure 1. The ± subscripting on n refers to the phasing of the $2p_y$ AO's on the two oxygen atoms. The subscript on $\pi_\oplus$ (Read: "pi circle plus") denotes the phasing of the carbon–carbon double bonds and implies that the MO has significant π amplitude on the oxygen centers. The meaning of the π_- notation is self-evident.

The He I photoelectron spectra (UPS) of PBQ and several of its derivatives have been reported.[3-5] Turner and co-workers[3a] have assigned the two n ionization events to the first UPS band in the 10.0–10.5-eV region (see Figure 2). Unfortunately, they cited no reasons for this assignment. Brundle and co-workers,[3b] during the course of their investigation of the "perfluoro effect", made a tentative assignment of the UPS of both PBQ and tetrafluoro-1,4-benzoquinone (TFPBQ). These latter assignments for PBQ, cited, per Koopmans' theorem,[6] in an MO energy basis, are: $n_u(n_+) > \pi_4(\pi_\oplus) > \pi_3(\pi_-) > n_g(n_-)$. The corresponing assignments for TFPBQ imply that the perfluoro effect shifts the n MO's to higher binding energy by ~5 eV—an amount which is clearly too large.

Cowan and co-workers[4] performed extended Hückel calculations on PBQ and assigned the MO's in the 10–11.5-eV UPS region as $n_- > \pi_4(\pi_\oplus) > n_+ > \pi_3(\pi_-)$. On this basis, the experimental splitting $\Delta n \equiv n_- - n_+$ is 0.9 eV for PBQ. Kobayashi[5] reported the UPS for PBQ, toluquinone (TQ), and 2,5-dimethyl-1,4-benzoquinone (25DMPBQ). On the basis of CNDO/2 calculations and certain empirical judgements, Kobyashi[5] concluded that the MO order for PBQ was that obtained by Cowan et al.[4] The net result of these last two works is that semi-empirical calculations of both the extended Hückel and CNDO/2 type produce an identical MO order for PBQ.

The purpose of the present work is to make an empirical assignment of the UPS of PBQ. Toward this end, we have studied the photoelectron spectra of PBQ and certain of its derivatives. The vibronic structure of UPS bands and substitution effects, particularly those produced by ring methylation, are used to correlate the UPS bands of different molecules. MO calculations are used sparingly and only in a perturbative sense: The electron densities on the various atom centers of PBQ, for example, may suggest that certain differential effects will be produced by substitutions of different types.

Experimental Section

The He I photoelectron spectra of PBQ, TFPBQ, 25DMPBQ, tetramethyl-1,4-benzoquinone (TMPBQ), tetrachloro-1,4-benzoquinone (TClPBQ), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DClDCNPBQ), 1,2,4,5-tetrachlorobenzene (TClBz), and hexachlorobenzene (HClBz) were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer. Resolution was 25 meV or better at the start of each spectral run. Xe and Ar were used as internal standards for calibration. The samples were obtained from commercial sources and were purified by vacuum sublimation. The temperature during each spectral run was maintained constant to within ±2 °C for those compounds that required heating to obtain enough vapor pressure to record a spectrum.

Semiempirical quantum chemical calculations were performed using the CNDO/2 routine.[2] Geometrical parameters were taken from electron diffraction data[7] for PBQ and benzene and form crystallographic data[7] for 25DMPBQ, TMPBQ, TClPBQ, TClBz, and HClBz. The geometrical parameters used for TFPBQ, 2,5-difluoro-1,4-benzoquinone, and DClDCNPBQ are also listed in ref 7.

Results and Discussion

A. 1,4-Benzoquinone (PBQ), 2,5-Dimethyl-1,4-benzoquinone (25DMPBQ), and Tetramethyl-1,4-benzoquinone (TMPBQ). The UPS of the low-energy region of PBQ, 25DMPBQ, and TMPBQ are shown in Figure 2. The ionization energies, vibrational frequencies, and assignments are listed in Table I.

The equal cross sections (i.e., relative band areas) of the two low-energy ionization bands in PBQ suggest that each band contains two ionization events, that is, one half of the total of four ionization events expected in this region. The origins of events $I(1)$ and $I(3)$ are quite intense and sharp and, as expected, the accompanying vibronic transitions are of much lower intensity. The second transition within each band is more diffuse: $I(2)$ is somewhat structured and possesses a definite vertical transition at 10.29 eV, while $I(4)$ is unstructured and partially hidden under $I(3)$.

Inspection of Figure 1 suggests that methylation of PBQ will destabilize the π orbitals, particularly π_-, more than the n orbitals, since the methylation occurs directly onto the carbon–carbon double bonds. The two bands comprising the low-energy region of PBQ converge as one proceeds toward TMPBQ. The decrease PBQ → DMPBQ is $\Delta\nu_{1/2} \simeq 0.2$ eV and DMPBQ → TMPBQ is $\Delta\nu_{1/2} \simeq 0.2$ eV, where $\Delta\nu_{1/2}$ is the *total* spectral half width of any spectrum of Figure 2. This observation suggests that the two π-orbital ionization events are contained in the second UPS band (i.e., that $I(3)$ and $I(4)$ of PBQ are $I(\pi)$ events).

The vibrational structure attributed to $I(3)$ in PBQ is retained in $I(4)$ of both 25DMPBQ and TMPBQ, and provides an unambiguous correlation of these ionization events. If we retain our initial assumption (i.e., that both the π ionizations are contained in the second UPS band of PBQ), the inversion of orbital ordering which is suggested by the spectral data of

Table I. Vertical Ionization Energies (eV)[a] of 1,4-Benzoquinone, 2,5-Dimethyl-1,4-benzoquinone, Tetramethyl-1,4-benzoquinone, and Tetrafluoro-1,4-benzoquinone

	$I(1)$	$I(2)$	$I(3)$	$I(4)$
PBQ	9.99	10.29	10.93	11.1 ± 0.1
MO assignment	n_-	n_+	$\pi_\oplus$	π_-
$\gamma(D_{2h})$	b_{3g}	b_{2u}	b_{3u}	b_{1g}
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	725 1500	700	1600	
25DMPBQ	9.60	10.05 ± 0.1		10.51
MO assignment	n_-	π_- and n_+		$\pi_\oplus$
$\gamma(C_{2h})$	a_g	b_g b_u		a_u
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	1500			1600
TMPBQ	9.25	9.50	9.75	10.02
MO assignment	n_-	π_-	n_+	$\pi_\oplus$
$\gamma(D_{2h})$	b_{3g}	b_{1g}	b_{2u}	b_{3u}
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)				1600
TFPBQ	10.96	11.21	11.3 ± 0.1	11.53
MO assignment	n_+	n_-	π_-	$\pi_\oplus$
$\gamma(D_{2h})$	b_{2u}	b_{3g}	b_{1g}	b_{3u}
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	1650	1350?[b]		1700

[a] All ionization events listed are ±0.05 eV unless otherwise indcated. The γ(point group) symbols refer to MO symmetries; the MO assignments are empirical and are largely based on the orbital pictures of Figure 1. [b] The question mark denotes our uncertainty as to whether the peak at 11.4 eV is either vibrational or the vertical component of the π_- ionization event.

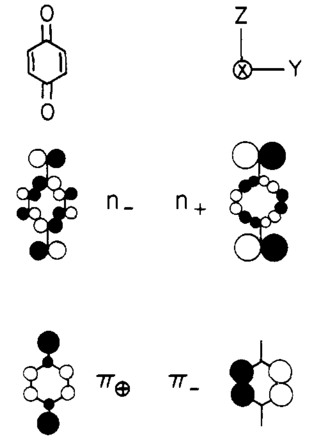

Figure 1. Pictorial representations of the four highest energy occupied MO's of 1,4-benzoquinone (PBQ) as generated by QCPE 141, CNDO/2. The diameter of the circular lobe is proportional to the size of the atomic orbital coefficient.

Figure 2 must originate in the π_- orbital of Figure 1: methylation must cause a larger destabilization of π_- than $\pi_\oplus$ because of the larger MO coefficients of the former on the centers of substitution.

The n_-/n_+ orbital energy splitting, Δn, can be estimated from that observed in the saturated analogue of PBQ (i.e., 1,4-cyclohexanedione[4]) for which $\Delta n \simeq 0.15$ eV. In any event, the Δn value in PBQ should not be larger than the 0.6-0.7-eV splitting found in 2,2,4,4-tetramethyl-1,3-cyclobutanedione[4,8] (TMCBD). Indeed, the value $\Delta n = 0.3$ eV for $I(2) - I(1)$ in PBQ seems to be quite reasonable.

The band shapes in PBQ, if $I(1)$ and $I(2)$ are assigned as the n-orbital ionization events, match those for TMCBD. In PBQ and TMCBD, the $I(1)$ events exhibit a coincidence of adiabatic and vertical transitions, and similar vibrational structures. The $I(2)$ events of PBQ and TMCBD are more nearly Gaussian, the vertical and adiabatic transitions being relatively well separated.

The methylation of PBQ to yield 25DMPBQ causes $I(2)$ and $I(3)$ of 25DMPBQ to meld into an unresolved feature. Since $I(1)$ and $I(4)$ of 25DMPBQ are uniquely correlatable, on the basis of vibronic structure, with $I(1)$ and $I(3)$, respectively, of PBQ, it follows that $I(2)$ and $I(3)$ of 25DMPBQ are related to $I(2)$ and $I(4)$ of PBQ. The two n MO's of 25DMPBQ are destabilized relative to PBQ, n_- being more affected than n_+, with the result that Δn increases to ~0.5 eV. This observation accords with conclusions drawn from Figure 1: n_+ has less electron density on the carbon skeleton and, hence, it should be influenced less by methylation than n_-.

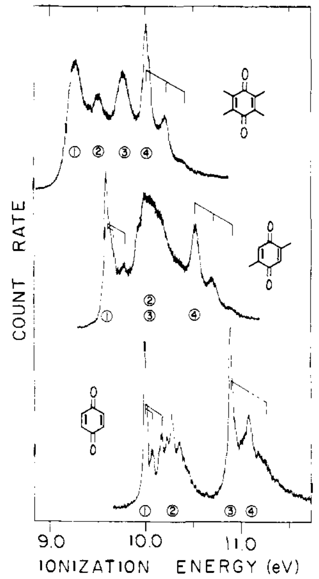

Figure 2. The expanded scale He I photoelectron spectra of 1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, and tetramethyl-1,4-benzoquinone. Vibrational spacings indicated on the spectra are listed in Table I along with the vertical ionization energies.

All four ionization events are resolved in the UPS of TMPBQ. Since methylation has increased Δn to ~0.5 eV in 25DMPBQ, and since methylation should also destabilize π_- more than either n_+ or n_-, the ionization events $I(2)$ and $I(3)$ of TMPBQ are best assigned as π_- and n_+, respectively. Thus, on proceeding from PBQ to TMPBQ, the π_- orbital has gone from the most tightly bound MO to the second most loosely bound MO of the set.

Further evidence in support of these assignments is provided by the additive effects of methylation. The additive effect[8,9]

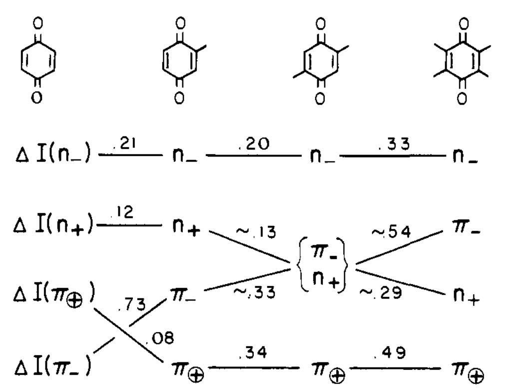

Figure 3. Schematic of the ionization energy differences between corresponding orbitals for 1,4-benzoquinone, toluquinone,[5] 2,5-dimethyl-1,4-benzoquinone, and tetramethyl-1,4-benzoquinone (note that Kobayashi's assignment[5] for toluquinone has been altered to accord with the interpretation presented here).

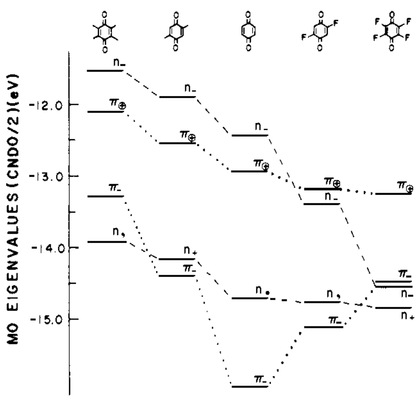

Figure 5. CNDO/2 correlation diagram for tetramethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 1,4-benzoquinone, 2,5-difluoro-1,4-benzoquinone, and tetrafluoro-1,4-benzoquinone.

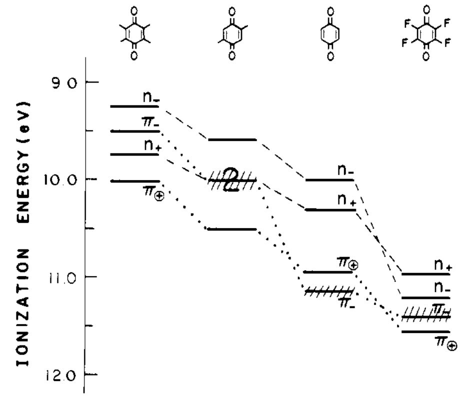

Figure 4. UPS correlation diagram for tetramethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 1,4-benzoquinone, and tetrafluoro-1,4-benzoquinone.

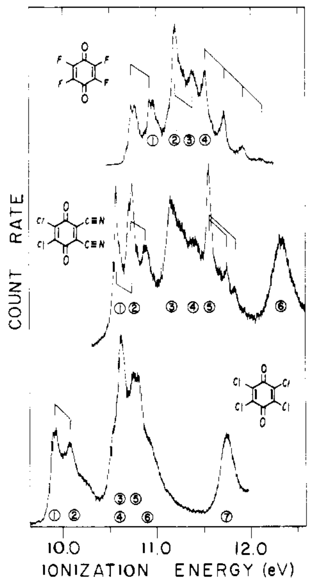

Figure 6. The expanded scale He I photoelectron spectra of tetrafluoro-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and tetrachloro-1,4-benzoquinone. Vibrational spacings indicated on the spectra are listed in Tables I and II along with the vertical ionization energies.

of methylation on the n-orbital ionization energies of monocarbonyls is well documented. That such additivity should also be evidenced by such a symmetrical molecule as PBQ is not unreasonable. The ΔI values for PBQ, TQ, 25DMPBQ, and TMPBQ are shown in Figure 3. The data of Kobayashi[5] for toluquinone were used in constructing Figure 3 (Note, however, that we have changed Kobayashi's assignments[5] to accord with our own predilections). The ΔI(n) values remain reasonably constant: $\Delta I(\mathrm{n}_-)$ decreases whereas $\Delta I(\mathrm{n}_+)$ increases slightly with progressive methylation.

The variations of $I(\pi_-)$ and $I(\pi_\oplus)$ are also included in Figure 3. Although certainly not additive, the behavior of $\Delta I(\pi_-)$ is readily rationalized: methylation decreases the LCAO coefficients on carbon atoms by providing another center, the -CH$_3$ group, on which the charge can "spread out", and by reducing the symmetry and, hence, allowing π_- density to appear on the carbonyl units. The resulting decrease in electron density on the remaining unmethylated carbon centers parallels, in a qualitative way, the observed decrease in $\Delta I(\pi_-)$. The behavior of $\Delta I(\pi_\oplus)$ is puzzling: that monomethylation should produce a small effect, whereas substitution of a second methyl group should produce a much larger effect is not inherent in the $\pi_\oplus$ MO diagram of Figure 1. If, however, we neglect the TQ data and fixate on the series PBQ → 25DMPBQ → TMPBQ, it is found that $\Delta I(\pi_\oplus)$ is roughly additive.

Trommsdorff[10] has also commented on the magnitude of the n-orbital splitting in PBQ. Trommsdorff analyzed the UV-vis absorption spectra of PBQ and derivatives. He concluded that a value $\Delta n \simeq 0.2$ eV for PBQ was reasonable, and he suggested that the previous assignment,[4] for which $\Delta n \simeq 0.9$ eV, should be reconsidered.

Our conclusion concerning PBQ, 25DMPBQ, and TMPBQ are presented in the correlation diagram of Figure 4. The results of the CNDO/2 MO calculations are shown in Figure 5. It is interesting that, whereas the calculated MO energies are particularly poor, the relative changes in orbital energies caused by substitution are more faithfully represented. In particular, the π_- MO is shown to be the most strongly affected by methylation.

B. Tetrafluoro-1,4-benzoquinone (TFPBQ). The UPS of TFPBQ is shown in Figure 6. It is quite different from the UPS of Figure 2. This difference is probably responsible for the dearth of comment on this molecule. The sole assignment available is that of Brundle et al.,[3b] which relies on a perfluoro shift of $\Delta I(\mathrm{n}) \simeq 5$ eV—by far the largest such shift ever suggested.

With the availability of reasonable, empirical assignments for PBQ and certain of its methyl derivatives, a starting point exists for the analysis of the UPS of TFPBQ. Our analysis of this spectrum is vested in three observations: (1) vibronic similarity of the $I(4)$ band of TFPBQ with the $\pi_\oplus$ bands of PBQ, 25DMPBQ, and TMPBQ; (2) orbital energy shift pat-

Table II. Vertical Ionization Energies (eV)[a] of Tetrachloro-1,4-benzoquinone, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, 1,2,4,5-Tetrachlorobenzene, and Hexachlorobenzene

	$I(1)$	$I(2)$	$I(3)$	$I(4)$	$I(5)$	$I(6)$	$I(7)$
TClPBQ	9.90	10.1 ± 0.1	10.65		10.8 ± 0.1	11.0 ± 0.1	11.8
MO assignment	n_-	n_+	π_- and $\pi_\oplus$				
$\gamma(D_{2h})$	b_{3g}	b_{2u}	b_{1g}	b_{3u}			
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	1300						
DClDCNPBQ	10.58	10.76	11.20	11.4 ± 0.1	11.58	12.4	
MO assignment	n_-	n_+	$\pi_\oplus$	π_-			
$\gamma(C_{2v})$[b]	b_2	a_1	b_1	b_1			
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	1200[c] or 1450	1200 ± 100			1350 and 1750		
TClBz	9.20[d]	9.67	11.21	11.68	11.96	12.15	12.49
MO assignment	π	π	n_{Cl}				
$\gamma(D_{2h})$	b_{1g}	b_{2g}					
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	320 and 1130	1250	1130				
HClBz	9.31[e]	10.95	11.06	11.67	11.90	12.20	12.35
MO assignment	π	n_{Cl}	n_{Cl}				
$\gamma(D_{6h})$	e_{1g}						
$\bar{\nu}_{vib}$ (cm^{-1}, ±50)	320 and 1210		1210				

[a] All ionization energies listed are ±0.05 eV unless otherwise indicated. The γ(point group) symbols are MO symmetry labels; the MO assignments are empirical and are based on MO pictures of Figure 1. The heavy mixing of the Cl "lone pair" orbitals with the PBQ orbitals renders the designations n_+, n_-, $\pi_\oplus$, and π_- only approximately descriptive of the orbital composition in the chlorinated derivatives. [b] The symmetry axes devolve from $D_{2h} \rightarrow C_{2v}$ as $x \rightarrow x$, $y \rightarrow z$, and $z \rightarrow y$. [c] The 10.76-eV peak contains a shoulder at 10.73 eV. It seems apparent that one of these two entities is a vibrational member built on the 10.58-eV origin; thus, the vibrational listing as either 1200 or 1450 cm^{-1}. [d] This value is one vibrational quantum of energy, 1130 cm^{-1}, higher than the value 9.06 eV reported by Streets and Caesar.[12] [e] This value is 1210-320 cm^{-1} higher in energy than the 9.20-eV value reported by Streets and Caesar.[12]

terns suggested by CNDO/2 computations[2] and based on the empirical assignment of PBQ; and (3) band shape comparisons with TClPBQ and DClDCNPBQ.

The UPS of the low-energy regions of TFPBQ, TClPBQ, and DClDCNPBQ are presented in Figure 6. The ionization energies and vibrational frequencies are listed in Table I for TFPBQ and in Table II for TClPBQ and DClDCNPBQ. The most noticeable feature of the UPS of TFPBQ is the vibrational progression of ~1700 cm^{-1} beginning at 11.53 eV. We identify this feature with the $\pi_\oplus$ band of PBQ. This done, considerations of the relative cross sections (i.e., band areas) suggest that four ionization events are contained in the low-energy region of TFPBQ. The structures at 10.76 and 10.96 eV constitute one single electronic ionization event and are of interest because of the band shape, which is unusual and without precedent in either PBQ or the methylated PBQ's. An origin with a band shape reminiscent of n_- of PBQ appears at 11.21 eV, and is so assigned. The remaining (or fourth) ionization event may be associated with the structure at 11.4 eV: while this structure may well be a vibronic feature built on the 11.21-eV origin, it is important to note that relative band area considerations do indicate the presence of two ionization events in the 11.2-11.4-eV range.

Some CNDO/2 results for PBQ, 25DMPBQ, TMPBQ, 2,5-difluoro-1,4-benzoquinone and TFPBQ are presented in Figure 5. Since we know that the relative MO order produced by the CNDO/2 algorithm is incorrect for the first four MO's, as are the Δn and $\Delta\pi$ splittings within each molecule, we will limit our use of Figure 5 to consideration of *trends* in the MO energies caused by substitution. For PBQ and its methyl derivatives, both the computational and experimental results indicate that all four orbitals are destablized by methylation, the π_- orbital being most sensitive. Fluorination is expected to stabilize all four orbitals. This expectation is borne out by computation (see Figure 5) for n_-, $\pi_\oplus$, and n_+, but not for π_-. If we suppose that the computed pattern of shifts is valid, a comparison of the observed spectra of TFPBQ (see Figures 4 and 6) and PBQ (see Figure 2) indicates that both the π_- and $\pi_\oplus$ events, and the n_- and n_+ events, have undergone energy inversions.

A comment on the use of the MO calculations is in order. Since the empirical correlations are fairly straightforward for PBQ, 25DMPBQ, and TMPBQ, and, to some extent, even for TFPBQ, we have chosen to invest primacy in them. The CNDO/2 results possess little utility but, where they do, they support the empirical assignments. We maintain that the residual utility of the CNDO/2 results consists only of the relative energy shifts *between different* molecules and not of the MO order or spacings *within any one* molecule. The one obvious exception to this perturbative use of CNDO/2 results is provided by the π_- orbital in the series PBQ → 25DFPBQ → TFPBQ: the π_- orbital does not destabilize upon fluorination; it simply stabilizes to a lesser extent than does $\pi_\oplus$ (see Figure 4).

The band shape of the lowest energy ionization event in TFPBQ has no precedent in any UPS spectrum discussed so far in this work. Consequently we have investigated the UPS of TClPBQ and DClDCNPBQ. The assignments for the two latter molecules will be presented in section C. Here, we content ourselves with the observation that the n_- and n_+ orbital ionization events correspond, respectively, to $I(1)$ and $I(2)$ in both TClPBQ and DClDCNPBQ. Very little can be learned from the band shape in TClPBQ. The spectrum of DClDCNPBQ, however, provides clear vibronic structure for the n_+ event: two peaks occur at ~10.76 and 10.9 eV, the high intensity of the 10.76-eV peak being due not only to the n_+ event, but also to a vibrational member associated with the n_- origin at 10.58 eV. (Note that even though 10.76 eV is the band

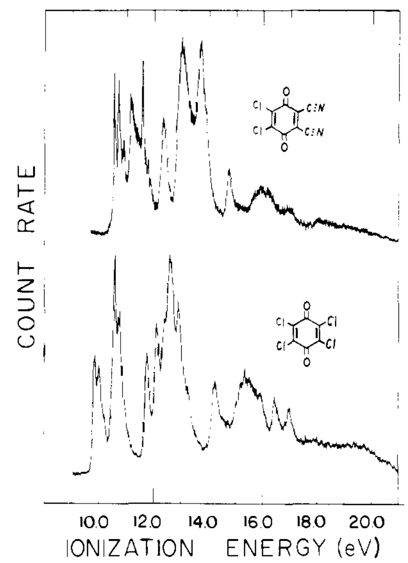

Figure 7. The He I photoelectron spectra of tetrachloro-1,4-benzoquinone and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

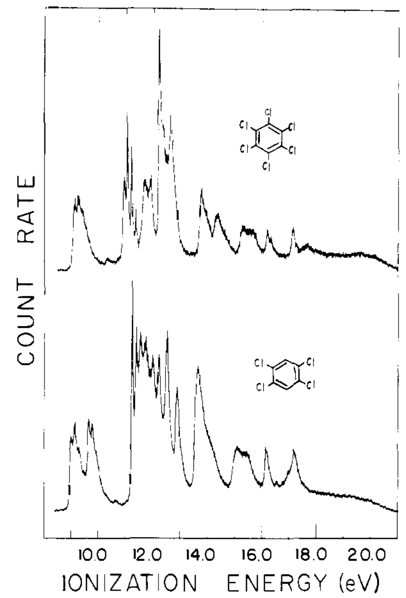

Figure 8. The He I photoelectron spectra of 1,2,4,5-tetrachlorobenzene and hexachlorobenzene.

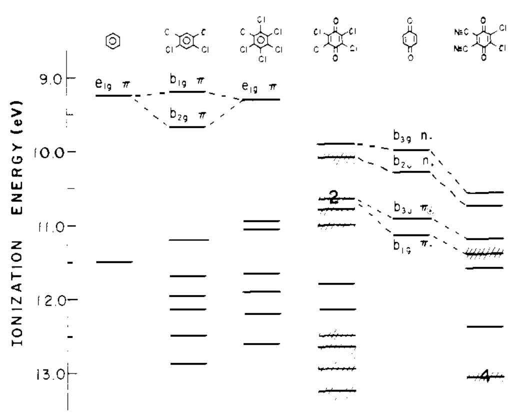

Figure 9. Correlation diagram based on UPS data for benzene,[11] tetrachlorobenzene, hexachlorobenzene, tetrachloro-1,4-benzoquinone, 1,4-benzoquinone, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

maximum, a quite definite structure also occurs at 10.73 eV. Which of these two bands is most properly associable with the 10.58-eV origin is not determinable.)

C. Tetrachloro-1,4-benzoquinone (TClPBQ) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DClDCNPBQ). The full He I UPS of TClPBQ and DClDCNPBQ are shown in Figure 7. Cross section considerations, based on the assumption that the band at 11.8 eV in TClPBQ represents a single orbital ionization event, indicate that two MO ionization events occur in the band at ∼10 eV, and that four such events occur in the band between 10.5 and 11 eV. For DClDCNPBQ, two MO ionization events are expected to lie within the structured band between 10.3 and 10.8 eV, three in the band from 10.9 to 12.0 eV, and one under the band at 12.4 eV. Obviously, the low-energy set of orbitals for these molecules consists of more than the two n and two π MO's pertinent for PBQ and TFPBQ.

Another problem is provided by the heavy mixing of the chlorine lone pairs—both n and π type—with the low-energy MO basis set of PBQ. We will continue to use the n and π orbital labels pertinent to PBQ and, as necessary, we will augment this set with chlorine n and π lone pair MO's. However, this is merely a convenience tactic which, we hope, does not cause confusion. The mixing of the low-energy MO set of PBQ with CH_3, F, and $C\equiv N$ orbitals is more or less negligible. Thus, the n_-, n_+, $\pi_\oplus$, and π_- nomenclature for PBQ, methylated PBQ's, and TFPBQ is totally meaningful. In particular, the lack of mixing of the $C\equiv N$ orbitals of DClDCNPBQ with the low-energy PBQ set makes this molecule akin to a 2,3-dichlorinated PBQ, at least insofar as the lower energy ionization events are concerned. Indeed, the highly electronegative nature of the $C\equiv N$ group should merely shift the low-energy MO ionization events of 2,3-DClPBQ to higher energy.

No clear empirical correlations of the UPS spectra of DClDCNPBQ or TClPBQ with that of PBQ is feasible. Consequently, in order to better comprehend chlorination effects, we have investigated the series benzene → 1,2,4,5-tetrachlorobenzene (TClBz) → hexachlorobenzene (HClBz). The topmost MO of benzene (D_{6h}) and HClBz (approximately D_{6h})[7] are formally degenerate. The UPS of benzene[11] is known. The He I UPS of TClBz and HClBz are shown in Figure 8. The lowest energy ionization(s) in these molecules (9–11 eV) is (are) known[12] to be π and to correspond to the e_{1g} MO of benzene, now heavily mixed with chlorine π type lone pair orbitals.

The correspondence of interest in these molecules is the effect of chlorination on the low-energy π orbitals. The assumption is made that the effect of chlorination on the low-energy π MO's of benzene—whether stabilization, destabilization, or a null effect—will be mimicked by similar effects of chlorination on PBQ. The empirical correlations of interest for the benzene series and the PBQ series are presented in Figure 9. The ionization data for TClBz and HClBz are listed in Table II.

The correlations of Figure 9 are quite clear. The lowest energy ionization event of benzene and HClBz are essentially identical. Additionally, two events, undoubtedly two Cl lone pair ionization events, occur at ∼11 eV in HClBz. Consequently, the correspondences between PBQ and TClPBQ become almost self-evident. The further correlation with the DClDCNPBQ data merely confirms the assignments. The very electronegative $C\equiv N$ groups, while contributing no low-energy ionization events of their own, delete one of the two "extra" ionizations expected for TClPBQ. The chlorine origin of the extra ionization events is thus demonstrated.

CNDO/2 MO calculations were also performed on this same set of molecules. No correlation of the calculated and experimental data was obvious. The disparity of the two data sets was quite extreme. Hence, we can offer no computational support for the empirical correlations of TClPBQ and DClDCNPBQ.

Conclusions and Remarks

The primary conclusions of this work are contained in the UPS data and assignments presented in Table l and ll. That these assignments are empirical is their greatest strength. It appears that parametrization of the CNDO/2 program is totally inadequate for PBQ and all of its derivatives.

From the absorption spectroscopic work of Trommsdorff,[10] we know the following: (i) that the ${}^1\Gamma_{n_-\pi^*}$ transition occurs at 20 060 cm^{-1} and the ${}^1\Gamma_{n_+\pi^*}$ transition occurs at 20 315 cm^{-1}; and (ii) that the exchange term, as measured by the singlet–triplet splitting, is very small, ~200 cm^{-1}, for both transitions. The energy splitting of the n_-/n_+ orbitals as determined here is 0.30 eV, while that for ${}^1\Gamma_{n_+\pi^*} - \Gamma_{n_-\pi^*}$ is 0.03 eV. To a first approximation, the 0.27-eV difference between the orbital energy split and the optical transition split must be caused by differences of the Coulomb intergrals, $J_{n_+\pi^*}$ and $J_{n_-\pi^*}$. To be in accord with the experimental data, $J_{n_+\pi^*}$ must be the larger of the two. Indeed, using the CNDO/2 generated LCAO-MO coefficients and a one-center approximation, we found $J_{n_+\pi^*}$ to be larger than $J_{n_-\pi^*}$. Thus, even a calculation at this crude level suggests that the energetic splitting of the ${}^1\Gamma_{n_-\pi^*}/{}^1\Gamma_{n_+\pi^*}$ transitions should be less than that of the n_-/n_+ orbitals, in accord with experimental observations.

This work, therefore, together with that of Trommsdorff, provides a very complete experimental determination of the electronic structure of PBQ.

PBQ is a relatively small, very symmetrical molecule which is of considerable biological importance.[13] Ab initio computational efforts, therefore, would appear to be mandatory. Two such efforts, in fact, are available in the literature.[14,15] Unfortunately, the crystallographic molecular structure[16] used in these computations differs considerably from the more recent electron diffraction[7] structure. Despite this, the agreement of both sets of computed results with the absorption spectroscopic data is very good; however, the ground state MO predictions, namely $\pi_\oplus > n_- > \pi_- > n_+$, are not in accord with photoelectron spectroscopy.

Finally, we reemphasize that the UPS assignments presented here do not accord with either semiempirical or ab initio computational results. The discord with semiempirical results is unfortunate and is undoubtedly correctable by reparametrization. The discord with the ab initio results may be a function of the nonoptimized, minimal basis-set nature of these calculations and the questionable geometry alluded to previously. The calculations by Cederbaum et al.[17] on formaldehyde suggest, however, that the breakdown of Koopmans' theorem may be more to blame. Nevertheless, it was this lack of computational support which provided the impetus for a rather complete empirical assignment. The calculated results of the vertical ionization energies for PBQ as per the method of Cederbaum et al.[17] would be welcome.

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References and Notes

(1) Other papers in this series include: J. L. Meeks, J. F. Arnett, D. Larson, and S. P. McGlynn, *Chem. Phys. Lett.*, **30**, 190 (1975); S. P. McGinn and J. L. Meeks, *J. Elecrron Spectrosc. Relat. Phenom.*, **6**, 269 (1975); J. L. Meeks, J. F. Arnett, D. B. Larson, and S. P. McGlynn, *J. Am. Chem. Soc.*, **97**, 3905 (1975); J. L. Meeks and S. P. McGlynn, *J. Electron Sepctrosc. Relat. Phenom.*, **8**, 85 (1976); J. L. Meeks, H. J. Maria, P. Brint, and S. P. McGlynn, *Chem. Rev.*, **75**, 603 (1975); J. L. Meeks and S. P. McGlynn, *Spectrosc. Lett.*, **8**, 439 (1975); J. L. Meeks and S. P. McGlynn, *J. Am. Chem. Soc.*, **97**, 5079 (1975); D. Dougherty, K. Wittel, J. Meeks, and S. P. McGlynn, *J. Am. Chem. Soc.*, **98**, 3815 (1976); D. Dougherty, J. J. Bloomfield, G. R. Newkome, J. F. Arnett, and S. P. McGlynn, *J. Phys. Chem.*, **80**, 2212 (1976).

(2) The semiempirical molecular orbital program used was QCPE 141, CNDO/2.

(3) (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Sepctroscopy", Wiley-Interscience, London, 1970; (b) C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, **94**, 1466 (1972).

(4) D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **10**, 401 (1971).

(5) T. Kobayashi, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 349 (1975).

(6) T. Koopmans, *Physica*, **1**, 104 (1934).

(7) For 1,4-benzoquinone: K. Hagen and K. Hedberg, *J. Chem. Phys.*, **59**, 158 (1973). For 2,5-dimethyl-1,4-benzoquinone: D. Rabinovich and G. M. J. Schmidt, *J Chem. Soc.*, 2030 (1964). For tetramethyl-1,4-benzoquinone: D. Rabinovich, G. M. J. Schmidt, and E. Ubell, *J. Chem. Soc. B*, 131 (1967). For tetrachloro-1,4-benzoquinone: S. S. C. Chu, G. A. Jeffrey, and (in part) T. Sakurai, *Acta Crystallogr.*, **15**, 661 (1962). For benzene: K. Kimura and M. Kubo, *J. Chem. Phys.*, **32**, 1776 (1960). For 1,2,4,5-tetrachlorobenzene: F. H. Herbstein, *Acta Crystallogr.*, **18**, 997 (1965). For hexachlorobenzene: I. N. Strel'cova and Jn. T. Struckov, *Zh. Strukt. Khim.*, **2**, 312 (1961) [*J. Struct. Chem.* (*Engl. Transl.*), **2**, 296 (1961)]. For tetrafluoro-1,4-benzoquinone and 2,5-difluoro-1,4-benzoquinone: the 1,4-benzoquinone skeletal geometry was used with a C–F bond distance of 1.32 Å. For 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: the tetrachloro-1,4-benzoquinone geometry, less the chlorine atoms at positions 5 and 6, was used; the cyano group bond lengths were 1.44 Å for the C–CN bond and 1.14 Å for the C≡N bond.

(8) Part of a dissertation presented to The Louisiana State University, Baton Rouge, Louisiana, by J. L. Meeks.

(9) J. L. Meeks, H. J. Maria, P. Brint, and S. P. McGlynn, *Chem. Rev.*, **75**, 603 (1975).

(10) H. P. Trommsdorff, *J. Chem. Phys.*, **56**, 5358 (1971).

(11) L. Åsbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970).

(12) O. G. Streets and G. P. Caesar, *Mol. Phys.*, **26**, 1037 (1973).

(13) R. A. Morton, Ed., "Biochemistry of Quinones", Academic Press, New York, N.Y., 1965.

(14) H. T. Jonkman, G. A. van der Velde, and W. C. Nieuwpoort, "Quantum Chemistry—The State of the Art", Proceedings of S. R. C., Atlas Symposium No. 4, 1974.

(15) M. H. Wood, *Theor. Chim. Acta*, **36**, 345 (1975).

(16) J. Trotter, *Acta Crystallogr.*, **13**, 86 (1960).

(17) L. S. Cederbaum, G. Hohlneicher, and S. Peyerimhoff, *Chem. Phys. Lett* **11**, 421 (1971).