

# On the Excited States of *p*-Quinones and an Interpretation of the Photocycloaddition of *p*-Quinones to Alkenes\*

Nigel J. Bunce, Joan E. Ridley and Michael C. Zerner

Guelph Waterloo Centre for Graduate Work in Chemistry,  
Dept. of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

A theoretical investigation is made of the electronic states of *p*-benzoquinone (PBQ), methyl substituted PBQ's and 1,4-naphthoquinone (NQ). In accord with experiment, the lowest triplet state of PBQ is calculated to be  ${}^3B_{1g}(n, \pi^*)$ , while that for duroquinone (DQ) is  ${}^3B_{3g}(\pi, \pi^*)$ . The electron densities of these states are consistent with the hypothesis that  ${}^3n, \pi^*$  states lead to oxetan formation and  ${}^3\pi, \pi^*$  states to cyclobutanes. It is predicted that trimethyl PBQ might form both adducts, as the two states are calculated to be nearly degenerate.

The photochemistry of NQ is more complex. The lowest excited triplet state is calculated to be of  $n, \pi^*$  symmetry, in accord with experiment; however, several other states are predicted near in energy, and the photochemistry cannot be rationalized unambiguously.

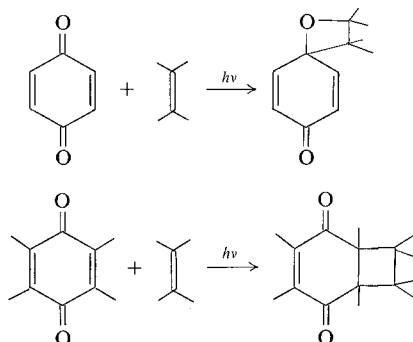
**Key words:** *p*-Quinones, photocycloaddition with alkenes – Electronic structure of *p*-quinones – Oxetans from  ${}^3n, \pi^*$  states of *p*-quinones – Cyclobutanes from  ${}^3\pi, \pi^*$  states of *p*-quinones – Spectra of quinones

## 1. Introduction

Like other saturated and unsaturated carbonyl compounds, *p*-quinones afford cycloadducts upon illumination in the presence of alkenes and related unsaturated substances [1–3]. Both oxetans and cyclobutanes have been observed, depending on the substituents present in the quinone, the former resulting from addition at the carbonyl group of the quinone, while the latter arise through addition at the C=C linkage. *p*-Benzoquinone (PBQ) itself reacts from a lowest triplet state [4] of the  $n, \pi^*$  configuration [5, 6] to yield exclusively oxetan adducts [7], while its

\* This work was supported in part by the National Research Council of Canada.

tetramethyl derivative duroquinone [DQ], whose lowest triplet state is  $\pi, \pi^*$  [5], affords only cyclobutanes [8].



It is thus attractive to propose that *p*-quinones whose lowest triplet state is  $n, \pi^*$  would react photochemically with alkenes to give oxetans, while cyclobutanes would result from the corresponding reactions of quinones whose lowest triplet state is  $\pi, \pi^*$  [9].

It is the purpose of this work to explore this hypothesis, both theoretically and experimentally. Of particular interest in this regard are quinones such as 1,4-naphthoquinone (NQ) [10] that are capable of forming both kinds of adducts simultaneously.

In the next section the quantum mechanical theories used to examine these systems are briefly described, as well as some strengths and shortcomings. Calculations and experiments are then discussed. In the PBQ series, the results are consistent with the hypothesis, but the complexities of the NQ system do not permit an unambiguous interpretation. However, NQ and trimethyl-*p*-benzoquinone are shown indeed to be candidates to form two (or more) adducts through nearly degenerate  $n, \pi^*$  and  $\pi, \pi^*$  excited triplet states.

## 2. Theory

In the calculation of electronically excited states of molecules, two general approaches have dominated; the Virtual Orbital Configuration Interaction method (VOCI) and the "energy difference" ( $\Delta E$ ) method. In the VOCI method the ground state is approximated by a single determinant (or a proper spin projection), built of the  $N$  lowest energy molecular spin orbitals, where  $N$  is the number of electrons. These orbitals are generally, but not always, of the self consistent field type. A basis of excited configurations is then built by exciting one or more electrons from these occupied orbitals to the virtual, or unoccupied orbitals, and these configurations are then used as the basis to describe molecular excited states, as well as to improve the description of the ground state.

An immediate advantage of this technique is that it provides an easy algorithm for calculating several of the lowest lying excited states at once. The disadvantage is that the occupied orbitals being used to describe the excited state have been optimized for the ground state. In addition, the virtual orbitals being populated are appropriate not for the  $N$  electron system, but the  $N + 1$  (negative ion) system and are, in general, too diffuse. The configurations thus obtained do not always provide a "good" starting point for the description of an excited state of interest, necessitating the inclusion of a great many determinants in the configuration interaction expansion, as well as an enlarged basis of orbitals.

In the "energy difference" technique ( $\Delta E$ ) two separate calculations of similar accuracy are performed, one on the ground state, and one on the excited state of interest, and the transition energy obtained by subtraction. These calculations are usually of the Hartree-Fock self-consistent field type, although they need not be. The advantages of this technique are that each state is separately optimized and that electronic rearrangements and relaxations are "built in". Apparent disadvantages are that a separate calculation is required for each excited state and that transition energies, small numbers, are obtained as the difference of two large numbers. With regard to the latter, difficulty may be encountered in trying to ascertain that each separate calculation is of "comparable" accuracy. For example, whereas the ground state of a molecule is well separated from excited states and may reasonably be represented by a single determinant (or proper spin combination), excited states often are not. If both calculations are of the restricted type [11], the ground state may be better treated than the excited states, for excited states are seldom well separated. If excited states are calculated in the unrestricted formalism [12], they may be relatively better treated than the ground state [13, 14].<sup>1</sup>

In this investigation, we have used both types of calculation. For the lowest lying excited triplet states, our experience indicates that the VOCI method, briefly described below, is most reliable in producing excitation energies in good accord with experiment. Once having identified these lowest triplet states, we would like to examine why each behaves photochemically as it does. To this end, separate SCF calculations on each excited state of interest preserve in a simple fashion the orbital picture that is lost in the VOCI calculations unless natural orbitals are obtained. In addition, in the  $\Delta E$  calculations, the relaxation of each excited state is considered in a natural way and thus one might expect to obtain more reliable charge distributions.

There is one final reason why we might wish to examine both types of results. Two different products can be obtained from the photoaddition of an ene to a quinone so that the actual product formed is a sensitive function of substituent, and in the case of naphthoquinone, temperature. It is therefore necessary to examine many states lying close in energy, and sometimes crossing. The quantum mechanical techniques available are not accurate enough to indicate with certainty which of

<sup>1</sup> In general, unrestricted wave functions can be expressed as expansions over restricted functions: see e.g. [13].

two near lying states is actually lower. Although we have usually found the transition energies calculated by the VOCI technique to be in good accord with experiment, typical uncertainties of  $\pm 2000 \text{ cm}^{-1}$  on each state may prove too large when comparing excited states close in energy. This is especially a problem when comparing  $n, \pi^*$  states, very well represented by our theories, with  $\pi, \pi^*$  states, generally calculated at higher energies than experimentally observed. We thus can use the  $\Delta E$  calculations to suggest possible reversals of excited states.

The calculations are performed using an Intermediate Neglect of Differential Overlap technique presented previously [15], and found accurate in describing the excited states of azanaphthalenes [16] and oxygen containing cyclic compounds [17]. The input to the program includes idealized crystallographic coordinates for NQ extrapolated from the work of Gaultier and Hauw [18a], and for PBQ from that of Trotter [18b]. After the self-consistent field calculation for the ground state has converged to within  $\pm 0.005$  electrons for each atom, the excited configurations are generated and interacted (CI) to form the excited states. The singlet CI includes all singly excited electronic configurations with energy within  $70,000 \text{ cm}^{-1}$  of the ground state (40–50 configurations); the triplet CI, all singly excited configurations within  $130,000 \text{ cm}^{-1}$  (80–120 configurations). State dipoles are calculated using the charge and one-centre polarization terms: oscillator strengths are calculated using the dipole length operator. The details of the singlet calculations can be found in Refs. [15] and [16]; of the triplet calculations in Refs. [17] and [19].

$\Delta E$  calculations are performed on those triplet states suggested by the VOCI results to be the lowest. These calculations are of the unrestricted type [12] and are performed with the same theory as employed for the VOCI results. As for the ground state, self consistency is assumed when each excited state has converged within  $\pm 0.005$  electrons for each atom. Convergence is not always assured, and an extrapolation procedure on the density is performed as described elsewhere [20].

Transition energies calculated by the VOCI technique refer to  $v_{\text{max}}$  values for reasons discussed elsewhere [15]. Since in the  $\Delta E$  method excited states are calculated at ground state geometries, these transition energies are also to be compared with  $v_{\text{max}}$  values.

### 3. Results

#### 3.1. Excited Singlet States

The VOCI calculations on the singlet states of PBQ, DQ and NQ are summarized in Table 1. In all cases, the two lowest lying excited singlets are  $n, \pi^*$  states. These states are estimated to be approximately 80% pure configurations, the lower of them representing the excitation of an electron from an orbital that is mainly the antibonding combination of the two oxygen lone pair orbitals to the lowest unoccupied MO ( $\pi$ ); the upper, from the plus combination to the same unoccupied  $\pi$  MO. As the interaction between these lone pairs is calculated to be weak, the separation of the two states is quite small. This is in agreement with observations

**Table 1.** Calculated and observed singlet states of quinones

Observed				Calculated			
Sym.	Type	Energy (cm <sup>-1</sup> )	f	Sym.	Type	Energy (cm <sup>-1</sup> )	f
<i>p</i> -Benzoquinone							
<sup>1</sup> B <sub>1g</sub>	<i>n</i> -π*	20,060 <sup>a</sup>		<sup>1</sup> B <sub>1g</sub>	<i>n</i> -π*	22,090	0.000
<sup>1</sup> A <sub>u</sub>	<i>n</i> -π*	20,315 <sup>a</sup>	0.0004 <sup>b</sup>	<sup>1</sup> A <sub>u</sub>	<i>n</i> -π*	23,142	0.000
<sup>1</sup> B <sub>3g</sub>	π-π*	32,800 <sup>a</sup>	0.008 <sup>b</sup>	<sup>1</sup> B <sub>3g</sub>	π-π*	32,585	0.000
<sup>1</sup> B <sub>1u</sub>	π-π*	41,330 <sup>a</sup>	0.15 <sup>b</sup>	<sup>1</sup> B <sub>1u</sub>	π-π*	42,526	0.882
Duroquinone							
<sup>1</sup> B <sub>1g</sub>	<i>n</i> -π*	20,702 <sup>c</sup>		<sup>1</sup> B <sub>1g</sub>	<i>n</i> -π*	23,019	0.000
<sup>1</sup> A <sub>u</sub>	<i>n</i> -π*	20,875 <sup>c</sup>		<sup>1</sup> A <sub>u</sub>	<i>n</i> -π*	23,920	0.000
		30,260 <sup>c</sup>	210 <sup>c</sup>	<sup>1</sup> B <sub>3g</sub>	π-π*	25,645	0.000
				<sup>1</sup> B <sub>1u</sub>	π-π*	38,702	0.771
1,4-Naphthoquinone							
<sup>1</sup> B <sub>1</sub>		23,161 <sup>d</sup>		<sup>1</sup> B <sub>1</sub>	<i>n</i> -π*	22,483	0.000
				<sup>1</sup> A <sub>2</sub>	<i>n</i> -π*	23,140	0.000
<sup>1</sup> A <sub>1</sub>		29,413 <sup>d</sup>		<sup>1</sup> A <sub>1</sub>	π-π*	31,300	0.155
				<sup>1</sup> B <sub>2</sub>	π-π*	31,908	0.028
<sup>1</sup> B <sub>2</sub>		40,592 <sup>d</sup>		<sup>1</sup> A <sub>1</sub>	π-π*	42,181	0.212
				<sup>1</sup> B <sub>2</sub>	π-π*	43,204	0.668

<sup>a</sup> Trommsdorff, H. P.: J. Chem. Phys. **56**, 5328 (1972):  $\nu_{00}$  values.

<sup>b</sup> Stevenson, P. E.: J. Mol. Spectry. **17**, 58 (1965).

<sup>c</sup> Braude, E. A.: J. Chem. Soc. 490 (1945):  $\nu_{\max}$  and  $\epsilon_{\max}$  values in *n*-hexane.

<sup>d</sup> Ref. [26]:  $\nu_{00}$  values.

made on PBQ and DQ. Interestingly, in none of these three compounds is an “*n*” MO calculated to be the highest occupied, although in each case they lie close in energy to the highest occupied  $\pi$  MO.

In all compounds we calculate a fairly large separation between the first  $\pi$ ,  $\pi^*$  bands and the lowest *n*,  $\pi^*$  states; this is in agreement with experiment. The smallest separation is found in DQ where a <sup>1</sup>B<sub>3g</sub>( $\pi$ ,  $\pi^*$ ) state is calculated at 25,645 cm<sup>-1</sup>, only 2600 cm<sup>-1</sup> above the lowest <sup>1</sup>B<sub>1g</sub>(*n*,  $\pi^*$ ).

The photocycloaddition of benzoquinones affords two products. With the possible exception of DQ the calculations and experiments suggest that in the singlet manifold, only the *n*,  $\pi^*$  states might be populated, collisional deactivation depopulating all other states before reaction can take place. These two *n*,  $\pi^*$  states, although they have different symmetries, are so similar (i.e., nearly identical charge distributions and dipole moments) that we consider them as very unlikely candidates to yield two different products. The following possibilities then remain: 1) each singlet *n*,  $\pi^*$  state yields two products, 2) one product results from the excited singlet, the other from a triplet, 3) both result from the same triplet, or 4) they result from two different triplets.

We would like to argue here against the first two possibilities. Experimentally, it

was first demonstrated for a variety of quinones that triplet states were the major participants in adduct formation. This involved sensitization and quenching studies of the kind previously described for PBQ itself [4], see Table 2. This result is in accord with common experience in the photochemistry of carbonyl compounds, which usually have quantum yields for intersystem crossing close to unity, and hence react from triplet rather than singlet excited states.

**Table 2.** Sensitization and quenching of quinone reactivity in the photolysis of *p*-quinones with cyclooctene

Quinone	Adduct [Ref.]	Relative rates		
		Direct irradiation	Sensitized irradiation	Quenched irradiation
Benzoquinone	Oxetan [7]	1.00	$1.06 \pm 0.13^{a, b}$	$0.43 \pm 0.02^{a, d}$
Duroquinone	Cyclobutane [8]	1.00	$1.16 \pm 0.02^b$	$0.11 \pm 0.10^e$
Anthraquinone	Oxetan [37]	1.00	$1.20 \pm 0.15^c$	$0.50^e$
Chloranil	Oxetan and cyclobutane [26] <sup>f</sup>	1.00	$0.87 \pm 0.02^b$	$0.53 \pm 0.05^d$
Naphthoquinone	Oxetan and cyclobutane [10]	1.00	$0.83 \pm 0.03^e$	$0.02 \pm 0.02^e$

<sup>a</sup> Data of Ref. [4].

<sup>b</sup> Benzophenone as sensitizer.

<sup>c</sup> Acetone as sensitizer.

<sup>d</sup> 9,10-Dibromoanthracene as quencher.

<sup>e</sup> Pyrene as quencher.

<sup>f</sup> Only cyclobutanes observed in present work, see text.

We would like to eliminate the first possibility on computational grounds also. From an examination of the charge density, the singlet  $n, \pi^*$  states might be possible precursors for oxetan formation (see later discussion), but there is no indication of any propensity to form cyclobutanes. Neither does the charge distribution of this state differ significantly from PBQ, the photochemistry of which yields oxetans, to duroquinone, which yields the cyclobutane adduct.

Possibility 2), that a singlet state is responsible for one product and a triplet for the other, seems unlikely in that it is difficult to understand why intersystem crossing for, say, DQ is much more efficient than that for PBQ itself. Suppose that DQ produces cyclobutanes through a triplet state, the singlet state being an unlikely precursor for reasons given previously. If PBQ forms oxetan from the singlet  $n, \pi^*$  state, and the rates of intersystem crossing are indeed similar, then why does photoexcited DQ not also produce some oxetan? Experimentally, DQ yields cyclobutanes with reported yields of up to 80%; oxetans were searched for but not detected [8]. Taking these arguments together, we suggest that both adducts are most likely produced through photo-populated triplet states.

### 3.2. Excited Triplet States

#### 3.2.1. *p*-Benzoquinone

An examination of the triplet spectrum of PBQ is summarized in Table 3. The

lowest triplet is  ${}^3B_{1g}(n, \pi^*)$  as found experimentally. This state is a likely precursor of an oxetan since the loss of electron density from the carbonyl oxygen should promote bond formation between oxygen and the alkene [4]. The results of  $\Delta E$  calculations are also reported in the table for three of the lowest four triplets. Qualitatively the results are very similar, with each  $\Delta E$  state calculated some 3000–4000  $\text{cm}^{-1}$  higher than its VOCI counterpart.

**Table 3.** Calculated and observed triplet states of *p*-benzoquinone

Observed			Calculated				
Symm.	Type	Energy	Symm.	Type	Energy		
					VOCI	$\Delta E$	
${}^3B_{1g}^c$	$n-\pi^{*c}$	$\nu_{00} = 18,370^c$ $\nu_{\max} \sim 20,000^{a,b}$	${}^3B_{1g}$	$n-\pi^*$	21,912	25,412	reactive state <sup>d</sup> ↑ 6280 $\text{cm}^{-1}$ (VOCI) 6349 $\text{cm}^{-1}$ ( $\Delta E$ ) ↓ reactive state <sup>d</sup>
${}^3A_u^c$	$n-\pi^{*c}$	$\nu_{00} = 18,683^c$	${}^3A_u$	$n-\pi^*$	23,742		
${}^3B_{1u}$	$\pi-\pi^{*c}$		${}^3B_{1u}$	$\pi-\pi^*$	27,195	29,919	
			${}^3B_{3g}$	$\pi-\pi^*$	28,192	31,761	

<sup>a</sup> Ref. [5].

<sup>b</sup> Ref. [29].

<sup>c</sup> Trommsdorff, H. P.: J. Chem. Phys. **56**, 5328 (1972); Trommsdorff claims that the first 2 triplets ( ${}^3B_{1g}$ ,  ${}^3A_u$ ) lie below the first singlet ( ${}^1B_{1g}$ ) ( $\nu_{00}$  values).

<sup>d</sup> The states thus indicated are the ones discussed in the text.

**Table 4.** Charge (and spin densities) for *p*-benzoquinone

	${}^1A_{1g}$ (Grd)	${}^3B_{1g}(n, \pi^*)$	${}^3B_{3g}(\pi, \pi^*)$	${}^3B_{1u}(\pi, \pi^*)$
<i>Net charges</i>				
O	-0.59	-0.49 (0.50)	-0.67 (0.18)	-0.46 (0.54)
C <sub>1</sub>	0.53	0.45 (0.23)	0.42 (0.09)	0.36 (0.06)
C <sub>2</sub>	-0.05	-0.06 (0.12)	0.04 (0.40)	-0.02 (0.20)
H	0.08	0.09 (0.02)	0.08 (-0.01)	0.07 (-0.01)
<i>Total pi densities</i>				
O ( $\pi$ )	1.46	1.67 (0.16)	1.57 (0.17)	1.31 (0.54)
C <sub>1</sub> ( $\pi$ )	0.63	0.77 (0.17)	0.77 (0.07)	0.83 (0.07)
C <sub>2</sub> ( $\pi$ )	0.96	1.03 (0.08)	0.83 (0.38)	0.93 (0.19)
<i>Total pi bond orders</i>				
CO ( $\pi$ )	0.82	0.60	0.69	0.58
C <sub>1</sub> C <sub>2</sub> ( $\pi$ )	0.27	0.43	0.42	0.49
C <sub>2</sub> C <sub>3</sub> ( $\pi$ )	0.92	0.81	0.53	0.68

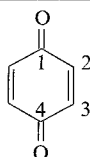


Table 4 presents the charge density and unpaired spin density for four states of PBQ obtained from the  $\Delta E$  results. As expected, the  ${}^3B_{1g}(n, \pi^*)$  has shifted density away from the oxygen. Orbital relaxation, however, has minimized this effect with only 0.1 electron actually "leaving" each oxygen. The C–O pi bond has considerably weakened from nearly pure doubled bond. This, coupled with the very large unpaired spin density on these two atoms, is very suggestive of oxetan formation.

If one tries to interpret these results in light of frontier orbitals, the analysis is very much *a posteriori*. Nevertheless, such analyses will aid in subsequent discussions on the more complex photochemistry of NQ, and we pursue it here. The highest occupied molecular orbital of the  ${}^3B_{1g}(n, \pi^*)$  state (and with unpaired  $\alpha$  spin) is of  $b_{2g}(\pi)$  symmetry, possesses a node through the carbonyl group, and could donate electrons to the ene antibond, Fig. 1. From the energy level diagram, more advantageous is ene bond donation to the unpaired  $\beta$  spin molecular orbitals. Both  $b_{3g}(n)$  and  $b_{2g}(\pi)$ , however, have nodes through the carbonyl group which would preclude such an interaction.

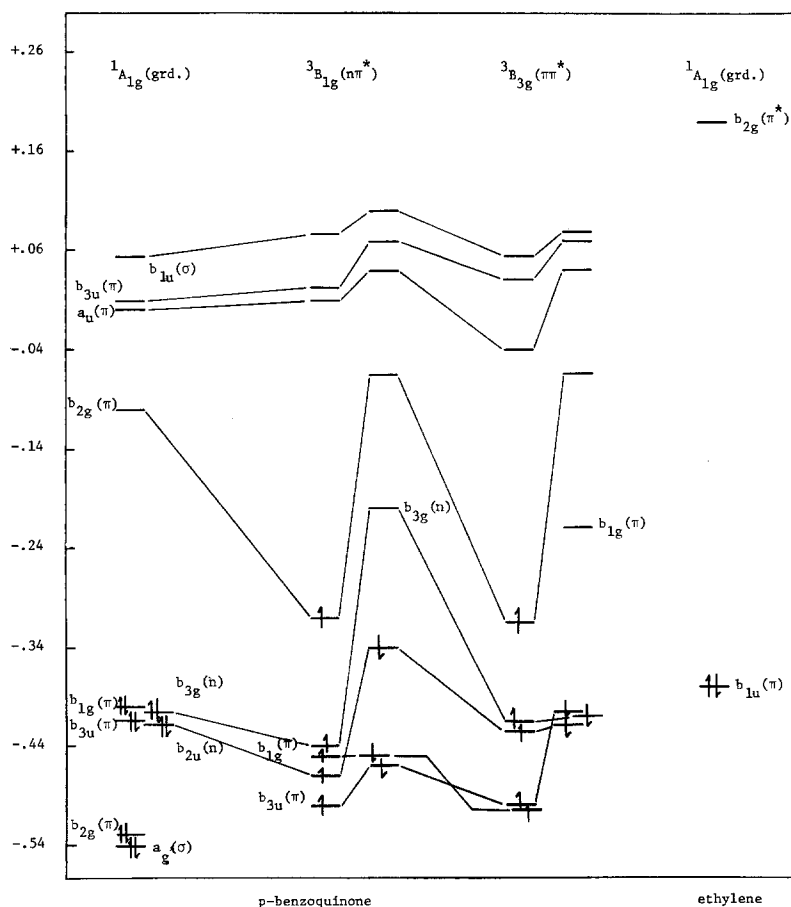


Fig. 1. Orbital energy level diagram of *p*-benzoquinone



## 3.2.2. Duroquinone

The triplet calculations on DQ are summarized in Table 5. The lowest triplet is  ${}^3B_{3g}(\pi, \pi^*)$ , calculated at  $22,134 \text{ cm}^{-1}$ , to be compared with an experimental  $\nu_{\max} \geq \nu_{00} \sim 19,000 \text{ cm}^{-1}$  [5, 6]. This state we assign responsible for the cyclobutane adduct. Examining Table 4 and assuming similar electronic structures for  $D_{2h}$  PBQ and DQ, this state shows a greatly weakened  $C_2-C_3$  ( $\pi$ ) bond and large spin densities at atoms  $C_2$  and  $C_3$  (and their symmetry equivalents). These points are highly suggestive that the  ${}^3B_{3g}(\pi, \pi^*)$  state is the precursor of the cyclobutane.

**Table 5.** Calculated and observed triplet states of duroquinone

Observed			Calculated			
Symm.	Type	Energy	Symm.	Type	Energy	
		$\nu_{00} \sim 19,000^a$	${}^3B_{3g}$	$\pi-\pi^*$	22,134	reactive state <sup>b</sup>
			${}^3B_{1g}$	$n-\pi^*$	23,101	reactive state <sup>b</sup>
			${}^3B_{1u}$	$\pi-\pi^*$	24,730	
			${}^3A_u$	$n-\pi^*$	24,800	

<sup>a</sup> Refs. [5, 6]: The lowest band is reported to be  $\sim 6000 \text{ cm}^{-1}$  wide. <sup>b</sup> See text.

Table 5, however, suggests that the  ${}^3B_{1g}(n, \pi^*)$  state of DQ lies at only slightly higher energy than  ${}^3B_{3g}$ . Since no oxetan production has been noted for DQ, we suspect that the calculated separation between  ${}^3B_{3g}$  and  ${}^3B_{1g}$  may be too small. Experience in *ab initio* work [21, 22] and in our own work suggests that  ${}^3\pi, \pi^*$  states are generally calculated to be too high in energy. This would increase the  ${}^3\pi, \pi^* - {}^3n, \pi^*$  separation, and explain the unique product formation in the DQ system.

Regarding the assignment of the lowest triplets, we must caution that triplet states are much more sensitive to the amount of configuration interaction than the corresponding singlets. The calculations on triplet states reported in the tables include configurational mixing of all pure single excitations lying within an energy of  $130,000 \text{ cm}^{-1}$  of the ground state, and appear stable towards inclusion of further excitations. Wood [23] encountered similar difficulties in *ab initio* calculations of the triplet states of PBQ. There too, the singlet transition energies appear relatively stable after a small configuration interaction (CI), but the triplets are not. In fact, his best CI suggests that the  ${}^3\pi, \pi^*$  state lies lowest, contrary to experiment. (Certainly, however, the lowest  ${}^3n, \pi^*$  and  ${}^3\pi, \pi^*$  states lie relatively close in energy.) Wood has also calculated the positions of the excited triplets by the  $\Delta E$  method. Again these calculations are ambiguous, with the lowest state obtained depending on the details of the calculation. Although we obtain better numerical agreement between the calculated and experimentally available energies of both singlet and triplet levels, we must again admit to an inherent uncertainty of at least  $4000 \text{ cm}^{-1}$  when comparing the energy differences between two different excited states.

An examination of the  ${}^3B_{3g}(\pi, \pi^*)$  frontier orbitals suggests that the highest occupied orbital of  $\alpha$  symmetry of the quinone,  $b_{2g}(\pi)$ , can interact favourably with the ene antibond as can the ene bond with the  $b_{1g}(\pi)$  unoccupied  $\beta$  spin MO of the quinone.

### 3.2.3. Other Methyl-*p*-benzoquinones

If one wishes to design a quinone capable of yielding both oxetan and cyclobutane photo-adducts, two procedures are suggested. By continuity, one of the methyl substituted PBQ's might form both, as PBQ itself forms only oxetan, DQ, only cyclobutane. The other possibility is that NQ or 1,4-anthraquinone might do so, as by enlarging the conjugation the  $\pi, \pi^*$  excitation energies (gaps) should decrease more rapidly than the  $n, \pi^*$  excitation energy.

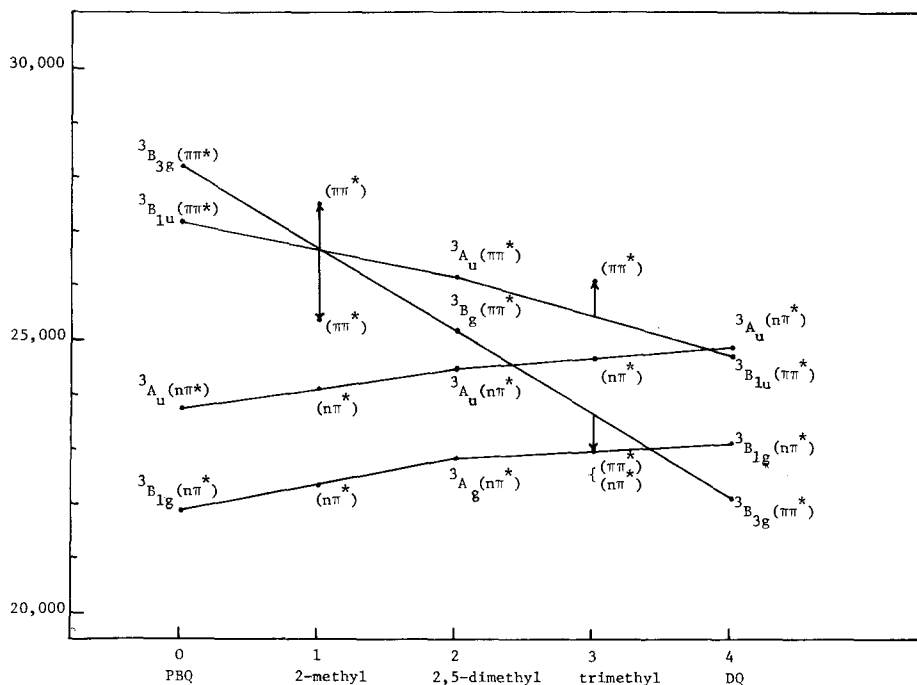
**Table 6.** Calculated triplet states of methyl-*p*-benzoquinones ( $\text{cm}^{-1}$ )

Symm. $D_{2h}$	Methyl PBQ		2,5 Dimethyl PBQ			Tri-methyl PBQ	
	Type	Energy	Symm.	Type	Energy	Type	Energy
${}^3B_{1g}$	$n-\pi^*$	22,307	${}^3A_g$	$n-\pi^*$	22,830	$n-\pi^*$	22,966
${}^3A_u$	$n-\pi^*$	24,030	${}^3A_u$	$n-\pi^*$	24,438	$n-\pi^*$	24,662
${}^3B_{3g}$	$\pi-\pi^*$	25,376 <sup>a</sup>	${}^3B_g$	$\pi-\pi^*$	25,110	$\pi-\pi^*$	23,011
${}^3B_{1u}$	$\pi-\pi^*$	27,474 <sup>a</sup>	${}^3A_u$	$\pi-\pi^*$	26,078	$\pi-\pi^*$	25,994

<sup>a</sup> These two states are heavy mixtures of the  $D_{2h}$   ${}^3B_{3g}$  and  ${}^3B_{1u}$  states, and thus cannot be correlated directly with PBQ states, see text.

An investigation of some of the methyl substituted PBQ's is summarized as Table 6, and Fig. 2. Most striking is the rapid decrease in energy of the  ${}^3B_{3g}(\pi, \pi^*)$  of PBQ as one successively adds methyl substituents. This decrease in excitation energy results mostly from an increase in the energy of the highest occupied orbital of pi symmetry, as each methyl carbon antibonds with the bonded carbon of the ring. In addition, each methyl carbon donates  $\sim 0.03$  electrons to the pi system of the ring, increasing the electrostatic repulsion. In contrast, the lowest unoccupied pi orbital involved in the transition has very little methyl character.

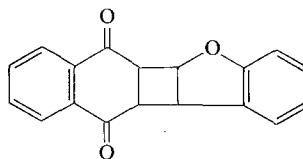
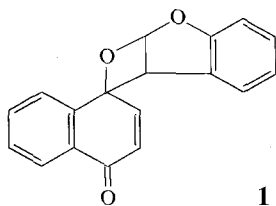
The lines in Fig. 2 connect states of similar symmetry. The pi states of methyl PBQ do not fall on these lines as the loss of symmetry causes the two corresponding states of PBQ, predicted nearly degenerate in methyl PBQ, to mix and repel one another. Trimethyl PBQ is somewhat similar, but the repulsion is not as great, for the corresponding pi states of DQ are predicted to be further apart. Trimethyl PBQ is predicted to be an excellent candidate to produce both oxetan and cyclobutane adducts. This prediction is even more appealing since our calculation of transition energies of  $\pi, \pi^*$  states is generally too high in relation to  $n, \pi^*$  states, as previously discussed. It might also be attractive, with this inherent uncertainty in mind, to speculate that one or more of the dimethyl PBQ's might also afford both adducts.



**Fig. 2.** Lowest excited states of PBQ and methylated PBQ's; solid lines connect states of similar symmetry. Arrows indicate the positions of  $\pi$ ,  $\pi^*$  states after configurational mixing due to reduced symmetry, see text

### 3.2.4. Naphthoquinone

The photochemistry of NQ is known to be complex, with both oxetan **1** and cyclobutane **2** adducts formed [10]. Our original idea, namely that this is because  $\pi$ ,  $\pi^*$  states should decrease in energy faster than  $n$ ,  $\pi^*$  states as we increase the conjugation from PBQ to NQ to 1,4-anthraquinone, does not seem to be a complete enough description. Table 1, for example, suggests that the lowest singlet



$n$ ,  $\pi^*$  state of NQ is actually higher in energy than the corresponding PBQ state. This is also true of the corresponding triplet states, Table 3 and 7. The lowest lying  $\pi$ ,  $\pi^*$  singlet, however, has come down somewhat in passing from PBQ to NQ.

The calculated triplet states are given in Table 7. The lowest excited triplet is  $n$ ,  $\pi^*$  in agreement with the experimental assignment based on fine structure in the

**Table 7.** Calculated and observed triplet states of 1,4-naphthoquinone ( $\text{cm}^{-1}$ )

Observed			Calculated							
Symm.	Type	Energy <sup>a, b</sup>	Symm.	Type	Energy					
					VOCI	$\Delta E$				
$^3A_2$	$n-\pi^*$	21,944	$^3B_1$	$n-\pi^*$	23,932	28,054	reactive state <sup>c</sup>			
			$^3A_2$	$n-\pi^*$	25,416	29,588	1932 ( $\Delta E$ )	4357 (VOCI)		
			$^3B_2$	$\pi-\pi^*$	28,289	29,986	reactive state <sup>c</sup>			
			$^3B_2$	$\pi-\pi^*$	29,339					
			$^3A_1$	$\pi-\pi^*$	30,164	29,886				
			$^3B_2$	$\pi-\pi^*$	36,393					

<sup>a</sup> Ref. [26]. <sup>b</sup>  $\nu_{00}$  values. <sup>c</sup> See text.

phosphorescence spectrum and the millisecond lifetime characteristic of such states [24, 25]. However, the calculations suggest a symmetry of  $^3B_1$  rather than  $^3A_2$  [26].

Although the VOCI results suggest that the  $n, \pi^*$  states are well separated from those of  $\pi, \pi^*$  type, the  $\Delta E$  calculations indicate that all may lie close in energy. Two quite different pictures thus emerge. The first, from the VOCI results, supports the existence of a single state yielding both products, while the second, from the  $\Delta E$  method, is consistent with the participation of two or more states.

Our preliminary efforts to choose between these two possibilities on experimental grounds did not lead to a clear cut distinction between them. Quenching studies, Table 8, suggested that differential quenching of the two states may be occurring (and hence that two or more different excited intermediates are involved), but the experimental uncertainties do not allow us to be confident about the conclusion. A

**Table 8.** Cyclobutane: oxetan ratio in the photoaddition of benzofuran to naphthoquinone

Solvent	Temp.	Conditions <sup>a</sup>	2/1
Benzene	Ambient	Direct irradiation	$0.84 \pm 0.03$
Benzene	Ambient	DBA quencher	$0.53 \pm 0.02$
Benzene	30°	Direct irradiation	$0.44 \pm 0.02$
Benzene	65°	Direct irradiation	$0.94 \pm 0.03$
Benzene	30°	TMD quencher	$0.37 \pm 0.05$
Benzene	65°	TMD quencher	$0.76 \pm 0.11$
$\text{CH}_3\text{CN}$	30°	Direct irradiation	$0.49 \pm 0.11$
$\text{CH}_3\text{CN}$	65°	Direct irradiation	$0.84 \pm 0.12$

<sup>a</sup> DBA is 9,10-dibromoanthracene; TMD is tetramethylazetidine, N,N-dioxide.

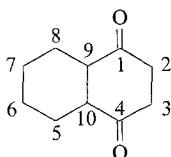
study of the effect of temperature on the ratio of products showed that more cyclobutane is formed at higher temperatures. Although this suggests a lowest oxetan-forming state with a thermally accessible state leading to cyclobutane at slightly higher energy, it does not eliminate the possibility of a single excited state with product distribution very sensitive to temperature change.

In support of a single state yielding both products is the observation that the product distribution does not greatly alter in changing solvent from non-polar benzene to polar acetonitrile, Table 8, since the  $n, \pi^*-\pi, \pi^*$  separation should be sensitive to solvent polarity. In near contradiction to the observation, however, and in support of the participation of several states in the photochemistry is the report that the triplet lifetime of NQ in the solid state is greatly lengthened, suggesting that under some conditions the triplet  $\pi, \pi^*$  may actually lie lower than the triplet  $n, \pi^*$  usually observed [10].

Results of a charge density study are presented in Table 9. The  ${}^3B_1(n, \pi^*)$  state of NQ appears quite similar to the  ${}^3B_{1g}(n, \pi^*)$  state of PBQ responsible for oxetan formation. The highest spin density resides on the atoms of the carbonyl group, and the C–O pi bond order is reduced from 0.80 to 0.59. The C<sub>2</sub>–C<sub>3</sub> spin density is

**Table 9.** Charge (and spin densities) for 1,4-naphthoquinone

	$A_1(\text{grd})$	${}^3B_1(n, \pi^*)$	${}^3A_2(n, \pi^*)$	${}^3B_2(\pi, \pi^*)$	${}^3A_1(\pi, \pi^*)$
Net charges					
O	-0.62	-0.52 (0.48)	-0.46 (0.55)	-0.65 (0.24)	-0.70 (0.20)
C <sub>1</sub> , C <sub>4</sub>	0.52	0.44 (0.24)	0.42 (0.22)	0.42 (0.07)	0.42 (0.11)
C <sub>2</sub> , C <sub>3</sub>	-0.04	-0.08 (0.16)	-0.08 (0.14)	-0.07 (0.06)	-0.07 (0.06)
C <sub>5</sub> , C <sub>8</sub>	0.00	-0.02 (0.04)	-0.03 (0.02)	-0.05 (-0.08)	0.19 (0.41)
C <sub>6</sub> , C <sub>7</sub>	-0.02	-0.03 (0.02)	-0.03 (0.02)	0.04 (0.31)	-0.05 (0.09)
C <sub>9</sub> , C <sub>10</sub>	-0.03	0.00 (0.06)	0.00 (0.04)	0.10 (0.40)	-0.02 (0.14)
Total pi bond orders					
CO	0.80	0.59	0.57	0.67	0.66
C <sub>1</sub> C <sub>2</sub>	0.28	0.47	0.48	0.41	0.43
C <sub>2</sub> C <sub>3</sub>	0.92	0.76	0.76	0.82	0.81
C <sub>4</sub> C <sub>10</sub>	0.30	0.39	0.40	0.42	0.40
C <sub>5</sub> C <sub>10</sub>	0.68	0.63	0.63	0.57	0.45
C <sub>5</sub> C <sub>6</sub>	0.61	0.66	0.66	0.73	0.50
C <sub>6</sub> C <sub>7</sub>	0.71	0.67	0.67	0.38	0.74
C <sub>9</sub> C <sub>10</sub>	0.57	0.55	0.55	0.25	0.58
Dipole moment (Debye) <sup>a</sup>					
	1.76	1.65	1.69	5.91	



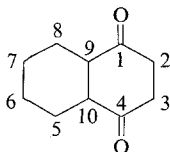
<sup>a</sup> The quinone moiety is the negative end of the dipole.

also high, higher than the corresponding state in PBQ, and the C<sub>2</sub>-C<sub>3</sub> pi bond order has dropped from 0.92 to 0.76, greater than the corresponding drop in PBQ. Thus it is conceivable that this state could also lead to cyclobutane. Nevertheless, 0.76 is still a large pi bond order, and it is difficult to understand why the <sup>3</sup>B<sub>1</sub> (*n*, π\*) state of NQ should yield both products, Table 8, while PBQ yields exclusively oxetan. Finally, we note that the highest occupied molecular orbital (HOMO) of the <sup>3</sup>B<sub>1</sub> (*n*, π\*) state can interact with the ene antibond for oxetan or cyclobutane formation, but the β spin lowest unoccupied molecular orbital (LUMO) cannot interact with the ene bond at either site. This is similar to what was found in the case of PBQ for oxetan only formation, cyclobutane formation being characterized by both HOMO and LUMO participation.

For these reasons we favour the second picture, that several triplet states are involved in the photochemistry of NQ. Table 10 summarizes the results of a study of the charge distributions and frontier molecular orbitals for the five triplet states calculated to lie so near in energy by the Δ*E* method. The two *n*, π\* states we assign to oxetan formation. The three π, π\* states are calculated to lie very close in energy by the Δ*E* method, and all suggest additions at carbon atoms. <sup>3</sup>A<sub>1</sub>, calculated lowest by Δ*E*, suggests 5,8 addition (Table 10); the lower <sup>3</sup>B<sub>2</sub>, 6,7 or 9,10 addition. Presumably these reactions would take place at the expense of resonance energy. Although there is more than enough energy available in these excited states to compensate for this, the simple picture we suggest for the reaction

**Table 10.** Adduct forming tendencies of the lowest triplets of 1,4-naphthoquinone<sup>a</sup>

	Highest density	Bonds most weakened	Adduct
<sup>3</sup> B <sub>1</sub> ( <i>n</i> , π*)	CO C <sub>2</sub> C <sub>3</sub>	CO C <sub>2</sub> C <sub>3</sub>	oxetan see text
<sup>3</sup> A <sub>2</sub> ( <i>n</i> , π*)	CO	CO	oxetan
<sup>3</sup> B <sub>2</sub> (π, π*)	C <sub>6</sub> C <sub>7</sub> C <sub>9</sub> C <sub>10</sub>	C <sub>6</sub> C <sub>7</sub> C <sub>9</sub> C <sub>10</sub>	6-7 cyclobutane 9-10 cyclobutane
<sup>3</sup> B <sub>2</sub> (π, π*) <sup>b</sup>	C <sub>2</sub> C <sub>3</sub>	C <sub>2</sub> C <sub>3</sub>	2-3 cyclobutane
<sup>3</sup> A <sub>1</sub> (π, π*)	C <sub>5</sub> C <sub>8</sub>	C <sub>5</sub> C <sub>10</sub> , C <sub>8</sub> C <sub>9</sub>	5-8 cyclohexene



<sup>a</sup> Results are from Δ*E* calculations unless noted. VOCI results appear to be similar.

<sup>b</sup> The second <sup>3</sup>B<sub>2</sub> cannot be obtained from an SCF calculation, but only the lowest state of each symmetry. The results reported here are from VOCI calculations.

is no longer valid. In addition, 9,10 and 6,7 addition yields dienes that might be expected to react further.

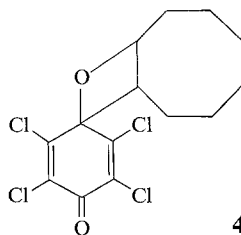
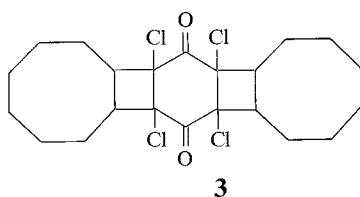
The second calculated  ${}^3B_2$  state is an excellent candidate to act as precursor to 2,3 addition. If this be the case, the barrier to reaction from the lower  ${}^3A_2$  or  ${}^3B_2$  must be sufficiently high to lead to state crossing, or the  ${}^3A_2$  may actually lie above this  ${}^3B_2$ . Since two near lying states are both of  ${}^3B_2$  character, it is also possible that the roles of these two states, so sensitive to configurational mixing, could be reversed by the addition of further CI. This, however, we doubt, as the distribution of charge in these two states is so very different.

Finally, numerous suggestions appear in the literature to the effect that exciplexes are involved in cycloadditions [27], including our own observations on oxetan formation from PBQ [4]. In the present case no reduction in the efficiency of photolysis was observed when the polarity of the reaction medium was changed from benzene to acetonitrile, lessening, although not necessarily eliminating, the need to invoke exciplexes as intermediates.

We conclude then, that at least two triplet states of NQ lie close enough in energy to be thermally populated within the lifetime of the triplet. Oxetans are formed from the lowest  ${}^3B_1$  ( $n, \pi^*$ ) state, and cyclobutanes from a slightly higher  ${}^3B_2$  ( $\pi, \pi^*$ ) state. Other adducts may also be present from populations in the  ${}^3A_2$  and other  ${}^3B_2$ , and these may undergo further Diels-Alder reactions. Such reactions will probably not be efficient as they will involve loss of resonance energy and thus, most likely, reaction barriers. These considerations are quite outside the scope of the present study; nevertheless, if so many excited states are accessible thermally, the activation energies may well be decisive in determining the reaction pathway actually followed. Attempts to pass barriers from lower states may actually populate higher lying states, thereby affording the 2,3 adduct.

### 3.3. Chloranil

It has been reported [28] that with cyclooctene as olefin, chloranil affords two kinds of adduct: a 2:1 cyclobutane **3** when the alkene is in excess, and a 1:1 oxetan **4** when a deficiency of the olefin is used.

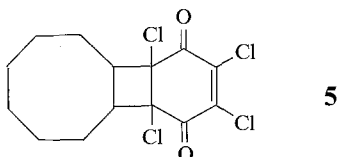


Experimentally, the lowest triplet state is believed to be  $\pi, \pi^*$  [29]. Although we have not performed calculations on chloranil, it is easy to rationalize this observation. Each chlorine is expected to donate electrons to the pi system of the quinone,

thus lowering the  ${}^3B_{3g}(\pi, \pi^*)$  state in a similar fashion to DQ. In addition, each chlorine atom withdraws electron density from the sigma orbitals of the quinone, and this should lower all the sigma symmetry MO's, including the  $n$  MO, thus raising the energy of the  ${}^3B_{1g}(n, \pi^*)$  level.

Our prediction then might be that the separation between the  ${}^3B_{1g}(n, \pi^*)$  and lowest  ${}^3B_{3g}(\pi, \pi^*)$  will be greater than that found for DQ. Since the latter only forms cyclobutane photo adducts, the observation that chloranil forms both becomes suspect.

Experiments on chloranil were performed, and will be reported in detail elsewhere. We find evidence for only the cyclobutane adducts **5** and **3**, consistent with the above arguments. Barltrop and Hesp [9] described an analogous 1:1 cyclobutane adduct from chloranil and isobutene.



#### 4. Conclusions

An examination has been made of the excited triplet states of *p*-benzoquinone (PBQ), methyl *p*-benzoquinone, 2,5-dimethyl-*p*-benzoquinone, tri-methyl-*p*-benzoquinone and duroquinone (DQ). Although the  ${}^3n, \pi^*$  lies lowest in PBQ, a  ${}^3\pi, \pi^*$  state is steadily reduced in energy upon methyl substitution until the latter is calculated nearly degenerate to the former in trimethyl PBQ and lower in DQ. Although there appears to be no experimental information on the triplet states of trimethyl PBQ, the lowest triplet state of DQ is observed to be  $\pi, \pi^*$ .

Calculations on 1,4-naphthoquinone (NQ) suggest that the lowest triplet is again of  $n, \pi^*$  character, in agreement with experiment. An examination of these calculations and the photochemistry of NQ, however, suggests several excited triplets lie very close in energy, all of which may be populated within the lifetime of the lowest triplet state. The observed products from the addition of an ene to photoexcited NQ are oxetan and 2,3-cyclobutane, but other reactions are possible from near lying states, all of which would presumably cost "resonance" energy. The question of whether one state or two different states lead to oxetan and cyclobutane in the case of NQ is not yet settled, though we have presented arguments favouring the latter interpretation.

In the case of chloranil, we suggest that only cyclobutanes should be formed photochemically, in contradiction to previous reports. Both kinds of adduct might be formed, however, by a less chlorinated derivative.

As the summary of results in Table 11 shows, there seems to be good reason for believing the original hypothesis, that oxetans are derived from quinones whose lowest triplet state is  $n, \pi^*$  while cyclobutanes are formed from lowest  ${}^3\pi, \pi^*$  states.



**Table 11.** Correlation of cycloadduct with lowest triplet state for *p*-quinones

Compound	Adduct	Lowest triplet
<i>p</i> -Benzoquinone	oxetan	$n, \pi^{*a}$
Duroquinone	cyclobutane	$\pi, \pi^{*a}$
Chloranil	cyclobutane	$\pi, \pi^{*b}$
Methoxy- <i>p</i> -benzoquinone	cyclobutane	probably $\pi, \pi^{*c}$
Naphthoquinone	both	$n, \pi^{*d}$
Anthraquinone	oxetan	$n, \pi^{*e}$

<sup>a</sup> This work and Ref. [5].

<sup>b</sup> Ref. [28].

<sup>c</sup> Pappas, S. P., Pappas, B. C.: Tetrahedron Letters 1597 (1967).

<sup>d</sup> This work and Ref. [25].

<sup>e</sup> Ref. [24, 25a, 25b].

This generalization appears to extend to other carbonyl compounds [30–36]. Within the *p*-quinone series, much experimental work remains to be done to confirm and test further the predictions of this theoretical study.

*Acknowledgement.* We are grateful to Mary Hadley for aiding in some of the experimentation reported here.

## References

- Bruce, J. M.: Quart. Rev. **21**, 405 (1967)
- Bryce-Smith, D., Fray, G. I., Gilbert, A.: Tetrahedron Letters 2137 (1964); Zimmermann, H. E., Craft, L.: Tetrahedron Letters 2131 (1964); Ishibe, N., Hashimoto, K., Yamaguchi, Y.: J. Chem. Soc. Perkin I, 318 (1975)
- Kuehne, M. E., Linde, H.: J. Org. Chem. **37**, 4031 (1972); Hassner, A., Blythin, D. J.: J. Org. Chem. **37**, 4209 (1972); Ishibe, N., Yamaguchi, Y.: J. Chem. Soc. Perkin I, 2618 (1973)
- Bunce, N. J., Hadley, M.: Can. J. Chem. **53**, 3240 (1975)
- Herre, W., Weis, P.: Spectrochim. Acta **29A**, 203 (1973); Kemp, D. R., Porter, G.: Proc. Roy. Soc. **326A**, 117 (1971)
- Sebti, M., Dupuy, F., Nouchi, G., Rousset, Y.: Compt. Rend. **270B**, 1477 (1970)
- Bryce-Smith, D., Gilbert, A., Johnson, M. G.: J. Chem. Soc. (C) 383 (1967)
- Schenck, G. O., Hartman, I., Metzner, W.: Tetrahedron Letters 347 (1965); Koltzenburg, G., Kraft, K., Schenck, G. O.: Tetrahedron Letters 353 (1965)
- Barltrop, J. A., Hesp, B.: J. Chem. Soc. (C) 1625 (1967)
- Krauch, C. H., Farid, S.: Tetrahedron Letters 4783 (1966); see also Maruyama, K., Olsuki, T., Takuwa, A., Kako, S.: Bull. Inst. Chem. Res., Kyoto Univ. **50**, 344 (1972), through Photochemistry: Specialist Periodical Report, The Chemical Society **4**, 406 (1974)
- Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951)
- Pople, J. A., Nesbet, R. N.: J. Chem. Phys. **22**, 571 (1954)
- Amos, T., Snyder, L. C.: J. Chem. Phys. **41**, 1773 (1964)
- Löwdin, P. O.: Advan. Chem. Phys. **2**, 207 (1959)
- Ridley, J. E., Zerner, M. C.: Theoret. Chim. Acta (Berl.) **32**, 111 (1973)
- Ridley, J. E., Zerner, M. C.: J. Mol. Spectry. **50**, 457 (1974)
- Ridley, J. E., Zerner, M. C.: unpublished results
- a) Gaultier, P. J., Hauw, C.: Acta Cryst. **18**, 179 (1965)  
b) Trotter, J.: Acta Cryst. **13**, 86 (1960)

19. Ridley, J. E., Zerner, M. C.: *Theoret. Chim. Acta (Berl.)* **42**, 223 (1976)
20. Bacon, A. D.: M.Sc. Thesis, University of Guelph, Guelph, Ontario (1976)
21. Del Bene, J. E., Ditchfield, R., Pople, J. A.: *J. Chem. Phys.* **55**, 2236 (1971)
22. Ditchfield, R., Del Bene, J. E., Pople, J. A.: *J. Am. Chem. Soc.* **94**, 703 (1972)
23. Wood, M. H.: *Theoret. Chim. Acta (Berl.)* **36**, 345 (1975)
24. Zander, M.: *Ber. Bunsenges. Phys. Chem.* **71**, 424 (1967); Singh, S. N., Singh, R. S.: *Indian J. Pure Appl. Physics* **5**, 394 (1967)
25. Dinh, T. V., Paetzold, R., Wild, U. P.: *Z. Phys. Chem. (Leipzig)* **251**, 395 (1972); Kuboyama, A., Matsuzaki, S.: *Tokyo Kogyo Shikensho Hokoku* **64**, 105 (1969); Shigorin, V. D., Shipulo, G. P.: *Zh. Prikl. Spektrosk.* **12**, 331 (1970)
26. Singh, S. N., Singh, R. S.: *Indian J. Pure Appl. Physics* **6**, 187 (1968)
27. Caldwell, R. A., Sovocool, G. W., Gajewski, R. P.: *J. Am. Chem. Soc.* **95**, 2549 (1973); Put, J., de Schryver, F. C.: *J. Am. Chem. Soc.* **95**, 137 (1973); Farid, S., Shealer, S. E.: *J. Chem. Soc. Chem. Commun.* 296 (1973); Yang, N. C., Eisenhardt, W.: *J. Am. Chem. Soc.* **93**, 1277 (1971); Turro, N. J., Wriede, P. A.: *J. Org. Chem.* **34**, 3502 (1969); Barltrop, J. A., Carless, H. A. J.: *J. Am. Chem. Soc.* **94**, 1951 (1972); Cantrell, T. S., Haller, W. S., Williams, J. C.: *J. Org. Chem.* **34**, 509 (1969); Challand, B. D., de Mayo, P.: *J. Chem. Soc. Chem. Commun.* 982 (1968)
28. Bryce-Smith, D., Gilbert, A.: *Tetrahedron Letters* 3471 (1964)
29. Sebti, M., Dupuy, F., Mège, J., Nouchi, G.: *Compt. Rend.* **272B**, 123 (1971)
30. Arnold, D. R., Hinman, R. C., Glick, A. H.: *Tetrahedron Letters* 1425 (1964); Yang, N. C.: *Pure Appl. Chem.* **9**, 591 (1964)
31. Magnifico, M., O'Connell, E. J., Fratini, A. V., Shaw, C. M.: *J. Chem. Soc. Chem. Commun.* 1095 (1972), and Refs. there cited; Cargill, R. L., Bundy, W. A., Pond, D. M., Sears, A. B., Salteil, J., Winterle, J.: *Mol. Photochem.* **3**, 123 (1971).
32. Chapman, O. L., Koch, T. H., Klein, F., Nelson, R. J., Brown, E. L.: *J. Am. Chem. Soc.* **90**, 1657 (1968)
33. Corey, E. J., Bass, J. D., LeMahieu, R., Mitra, R. B.: *J. Am. Chem. Soc.* **86**, 5570 (1964)
34. Yoshida, Z., Kimura, M., Yoneda, S.: *Tetrahedron Letters* 1001 (1975)
35. Barltrop, J. A., Giles, D.: *J. Chem. Soc. (C)* 105 (1969), and Refs. there cited
36. Still, I. J. W., Kwan, M.-H., Palmer, G. E.: *Can. J. Chem.* **46**, 3731 (1968)
37. Bryce-Smith, D., Gilbert, A., Johnson, M. G.: *Tetrahedron Letters* 2863 (1968)

*Received February 7, 1977*