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An *ab initio* CI study of the ground and excited states of *p*-quinodimethane

Tae-Kyu Ha

Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum,
CH-8092 Zurich, Switzerland

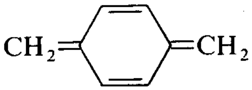
Configuration interaction (CI) studies of the ground, electronically excited singlet and triplet states and of the ionized states (cations) are reported for *p*-quinodimethane (*p*-xylylene). The calculated ionization potentials are compared with the experimental photoelectron spectrum for the low-energy ionization region. The two high-energy low-intensity flanks of the second and third band observed in the photoelectron spectrum are assigned to be due to the two non-Koopmans' cation states, ascribing to shake-up ionizations.

The calculated singlet–singlet and singlet–triplet excitation energies are compared with previous semiempirical MO results and experimental data.

Key words: *p*-xylylene—*ab initio* calculations—ionization potentials—excited states

1. Introduction

The transient species *p*-quinodimethane (PQD),



may be formed by flash vacuum thermolysis of its dimer, [2, 2] paracyclophane [1], and the vibrational and electronic spectra of the isolated species in the solid state at 77°K indicated the quinoid structure of this species [2]. The polymer of PQD is of technical interest with respect to durable coating polimeric materials research, and direct spectroscopic evidence of the polymerization process has been reported [2, 3].

The *uv* spectrum of PQD at 77°K was measured with $\lambda_{\max} = 301$ mμ [2], and the ionization potentials have been reported by the *uv* photoelectron spectroscopy by Koenig et al. [4].

Several theoretical studies of the electronic structure and spectra on PQD are also available in the literature [5–13]. All of these theoretical studies were based on the semiempirical MO schemes, except the one by Hiberty and Karafiloglou [5] which dealt with the estimates of the biradical character of quinodimethanes by the valence bond method employing the minimal basis set.

One of the most interesting problems of PQD, however, centered around the interpretation of the photoelectron spectrum, and various semiempirical MO studies provided some conflicting results.

The semiquantitative interpretation of the *uv* photoelectron spectrum is usually based on the Koopmans' approximation, which neglects the effects of electron reorganization and correlation. Koenig et al. [4] originally assigned the shoulder of low intensity at 9.8 eV (the third band) in the photoelectron spectrum of PQD to the HOMO–LUMO shake-up state, which arises from a pronounced configuration mixing between the Koopmans' state and the non-Koopmans' HOMO–LUMO valence excitation. Recently, Dewar rejected this assignment on the basis of the semiempirical MNDO SCF calculations [7], and the spectral feature in question was ascribed to an impurity. However, other recent semiempirical MO calculations based on MNDO, CNDO/S and LNDO/S [8, 9] and HAM/3 method [11, 13] indicated that the original assignment of Koenig et al. [4] was correct, showing that the configuration mixing is as important in the interpretation of the photoelectron spectrum of low energy region, as in the case of the inner valence high energy region.

In the present study, we report an extended configuration interaction (CI) calculation on the ground, excited and ionized states of PQD employing a gaussian basis set of double-zeta (DZ) quality, and try to resolve the existing discrepancies among earlier semiempirical MO studies especially with respect to the interpretation of the ionization potentials of this molecule.

Furthermore, the singlet→singlet and singlet→triplet excitation energies have been calculated and discussed in detail.

2. Details of the calculations

The *ab initio* self-consistent field (SCF) calculation which preceded the CI study employs the gaussian basis set of Huzinaga's ($9s, 5p$) set [14], contracted to a double-zeta (DZ) according to Dunning's scheme [15]. A ($4s$) gaussian expansion of the hydrogen $1s$ orbital with a scale factor 1.2 was similarly contracted to a ($2s$) set for each of eight hydrogen atoms [15].

The molecular geometry used in the calculation was assumed as alternately single and double bond lengths of 1.447 and 1.342 Å, respectively, with the C–H bond length of 1.09 Å. All bond angles of 120° were also assumed. These geometrical parameters are consistent with the optimized MNDO geometry of Dewar [7] as well as with those of other earlier theoretical studies [5, 9], representing the quinoid structure of PQD. The molecule has D_{2h} symmetry and lies in the xz plane, the z axis coinciding with the longer axis.

The SCF calculation has first been performed for the singlet ground state (^1A_g) resulting in the following configuration,

$$[\ldots(7b_{1u})^2(5b_{2u})^2(8a_g)^2(1b_{3u})^2(4b_{3g})^2(1b_{2g})^2(1b_{1g})^2(2b_{3u})^2],$$

with the SCF energy of −307.45982 a.u. The lowest lying virtual orbital (LUMO) corresponds to the $2b_{2g}(\pi^*)$ orbital.

In addition, the open-shell SCF calculations [16] have been carried out for the singlet and triplet excited and seven doublet cationic states resulting from ionizations of the occupied orbitals of the ^1A_g ground state configuration.

The DZ basis set calculation of PQD leads to 96 molecular orbitals, eight of which correspond to carbon 1*s* orbital. These eight orbitals were assumed to form a frozen core and were kept fixed. As orbitals of variable occupancy in the CI calculation, 60 valence orbitals have been employed, which include all π and π^* type orbitals (16 such orbitals) and 44 σ and σ^* type orbitals. As reference configuration in the CI calculation, the open-shell SCF configuration for the corresponding state has been employed in the calculation of the excited states. For the doublet cationic states, two reference configurations have been used; one which represents the Koopmans' configuration and the other representing the HOMO-LUMO excitations.

The CI calculation has been carried out for each state of interest by including all single and double excitations of the valence shell electrons from each reference configuration. The configurations were selected by perturbation theory with energy threshold of 5×10^{-5} a.u. Within the truncation of the MO bases and the perturbation threshold, the dimension of the CI wavefunction amounted to 2752 for the ground state with the CI energy of −307.64317 a.u.

3. Results and Discussion

The calculated MO energies and the total SCF and CI energies for the ground state of PQD are summarized in Table 1. The three higher lying MO's are all π-type orbitals and the highest occupied (HOMO) and the lowest unoccupied (LUMO) MO's correspond to the $2b_{3u}(\pi)$ and $2b_{2g}(\pi^*)$ orbitals, respectively. The CI energies, difference between the CI and SCF energies and the dimension of the CI wavefunctions for the cations of PQD considered in this study are listed in Table 2. As mentioned above, two reference configurations have been employed to obtain the CI wavefunctions and energies for the cationic states. The coefficients of the two reference configurations of these cations are summarized in Table 3. Examining the coefficients of the two reference configurations for each state, it is noted that the configuration mixing between the reference

Table 1. Calculated MO and total energies of *p*-quinodimethane[a]

MO energies			
$4a_g$	−1.1616	$3b_{3g}$	−0.5832
$4b_{1u}$	−1.0789	$7b_{1u}(\sigma)$	−0.5701
$2b_{2u}$	−1.0377	$5b_{2u}(\sigma)$	−0.5283
$5a_g$	−0.9842	$8a_g(\sigma)$	−0.5247
$5b_{1u}$	−0.8449	$1b_{3u}(\pi)$	−0.5133
$2b_{3g}$	−0.8266	$4b_{3g}(\sigma)$	−0.4751
$6a_g$	−0.7823	$1b_{2g}(\pi)$	−0.4118
$7a_g$	−0.6749	$1b_{1g}(\pi)$	−0.3713
$3b_{2u}$	−0.6682	$2b_{3u}(\pi)$	−0.2703 (HOMO)
$6b_{1u}$	−0.6521	$2b_{2g}(\pi^*)$	0.1405 (LUMO)
$4b_{2u}$	−0.6079		
E_T(SCF)	−307.45982		
E_T(CI)	−307.64317[b]		

[a] Double-zeta basis set: Atomic units. For the ground state, eight MO's which correspond to the core orbitals are omitted in the listing.
[b] Energy threshold of 5.10^{-5} a.u. has been employed

Table 2. Energies of the CI wavefunctions of the *p*-quinodimethane cation[a]

Electronic state	Main ionization	E(CI)	ΔE(CI–SCF)	Dimension
${}^1A_g(I)$	ground state	−307.64317	−0.18335	2752
${}^1A_g(II)$	$[(2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−307.40823		2752
${}^2B_{3u}(I)$	$[(2b_{3u})^1(\pi)]$	−307.38154	−0.17093	5174
${}^2B_{3u}(II)$	$[(1b_{3u})^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−307.16842		5174
${}^2B_{1g}(I)$	$[(2b_{1g})^1(\pi)]$	−307.30298	−0.15679	5531
${}^2B_{1g}(II)$	$[(2b_{1g})^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−307.08300		5531
${}^2B_{2g}(I)$	$[(1b_{2g})^1(\pi)]$	−307.29238	−0.21869	6133
${}^2B_{2g}(II)$	$[(2b_{2g}), (2b_{3u})^2 \rightarrow (1b_{2g})^2]$	−307.21392		6133
${}^2B_{3g}(I)$	$[(4b_{3g})^1(\sigma)]$	−307.23580	−0.21998	6780
${}^2B_{3g}(II)$	$[(4b_{3g})^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−306.98722		6780
${}^2A_g(I)$	$[(8a_g)^1(\sigma)]$	−307.19989	−0.23252	7274
${}^2A_g(II)$	$[(8a_g)^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−306.95114		7274
${}^2B_{2u}(I)$	$[(5b_{2u})^1(\sigma)]$	−307.17966	−0.23236	6866
${}^2B_{2u}(II)$	$[(5b_{2u})^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−306.98870		6866
${}^2B_{1u}(I)$	$[(7b_{1u})^1(\sigma)]$	−307.15721	−0.20792	7309
${}^2B_{1u}(II)$	$[(7b_{1u})^1, (2b_{3u})^2 \rightarrow (2b_{2g})^2]$	−306.95737		7309

[a] Atomic units. Energy threshold of 5.10^{-5} a.u. has been used

configuration representing the single ionization and that for the HOMO–LUMO interaction is distinctively pronounced for the ${}^2B_{2g}$ cationic state. The CI coefficients of the reference configuration representing the single ionization are only 0.70342 and 0.57918 for the two ${}^2B_{2g}$ states, leading to a complete breakdown in a Koopmans' theorem interpretation of the photoelectron spectrum for these states. For the other cationic states, the mixing of the reference configuration

Table 3. Coefficients of the CI-reference configurations for some lower lying state of the *p*-quinodimethane cation

	Reference configuration representing the single ionization	Reference configuration including the HOMO–LUMO interaction
^1A_g (ground state)	0.91248	0.18693
$^2B_{3u}(I)$	0.93175	0.11596
$^2B_{1g}(I)$	0.90783	0.20810
$^2B_{2g}(I)$	0.70342	0.59456
$^2B_{2g}(II)$	0.57918	0.66521
$^2B_{3g}(I)$	0.90442	0.17898
$^2A_g(I)$	0.90063	0.17852
$^2B_{2u}(I)$	0.89768	0.15950
$^2B_{1u}(I)$	0.89791	0.17010

Table 4. A summary of the calculated ionization potentials of *p*-quinodimethane (eV)

Electronic states	Main ionization	$-\varepsilon_i$	ΔE(SCF)	ΔE(CI)
$^2B_{3u}(I)$	$2b_{3u}(\pi)$	7.35	6.78	7.12
$^2B_{3u}(II)$		—	—	12.92
$^2B_{1g}(I)$	$2b_{1g}(\pi)$	10.10	9.10	9.27
$^2B_{1g}(II)$		—	—	15.24
$^2B_{2g}(I)$	$1b_{2g}(\pi)$	11.12	10.51	9.54
$^2B_{2g}(II)$		—	—	11.68
$^2B_{3g}(I)$	$4b_{3g}(\sigma)$	12.93	12.08	11.08
$^2B_{3g}(II)$		—	—	17.85
$^2A_g(I)$	$8a_g(\sigma)$	14.28	13.40	12.06
$^2A_g(II)$		—	—	18.83
$^2B_{2u}(I)$	$5b_{2u}(\sigma)$	14.38	13.95	12.61
$^2B_{2u}(II)$		—	—	17.80
$^2B_{1u}(I)$	$7b_{1u}(\sigma)$	15.51	14.71	13.22
$^2B_{1u}(II)$		—	—	18.66

including the HOMO–LUMO valence excitation is relatively small, and thus the parent one-electron Koopmans' state is clearly the dominant term.

The calculated ionization energies in the SCF and CI levels are summarized in Table 4 and a comparison between various levels of calculations and experiment has been made in Fig. 1.

The ionization potentials obtained by the ΔSCF method ($\Delta\mathrm{SCF} = E_{\mathrm{SCF}}$(ground state $- E_{\mathrm{SCF}}$(cation)), which incorporates the charge reorganization of the cationic state is found to be qualitatively similar to the negative MO energies (Koopmans' approximation), even though the absolute values are at variance with each other by up to 1 eV in all cases. We have previously shown that the Koopmans' approximation may lead to wrong results for strongly localized molecular orbitals

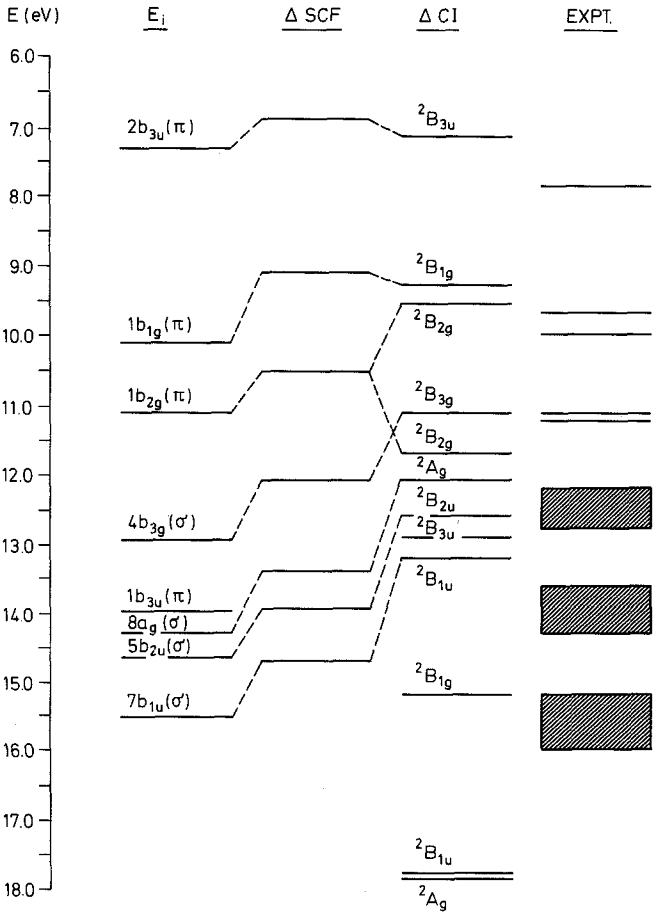


Fig. 1. A comparison of the calculated ionization potentials in the SCF and CI levels with the experiment (Ref. [4]). ε_i: orbital energy, ΔSCF: SCF energy difference between the cations and the ground state, ΔCI: CI energy difference between the cations and the ground state. The hatched area stands for the PES region between 12.0 to 16.0 eV, which has an irregular and difficult to understand fine structure

such as those of *p*-benzoquinone [17]. The first four bands of the photoelectron spectrum in *p*-benzoquinone may be assigned to n_g, n_u, π_u and π_g if configuration interaction is admitted, even though the MO ordering is π_u, π_g, n_g and n_u in order of increasing energy. A similar striking change in the energy ordering also takes place for PQD after the CI calculations, as shown in Table 4 and Fig. 1.

The first ionization potential may distinctively be assigned to the ionization from the π type $2b_{3u}$ orbital. The caluclated CI value of 7.12 eV is comparable to the experimental value of 7.78 eV [4]. The following two sets of doublet bands at about 10 and 11 eV observed in the experiment are two states of qualitatively different origin. While the lower energy part of the second band system calculated at 9.27 eV corresponds to the π ionization from the $1b_{1g}$ orbital, the high-energy flank of this band calculated at 9.54 eV may be assigned to the shake-up ionization, representing the first non-Koopmans' state occurring in PQD, as the CI coefficients of the two reference configurations indicate in Table 3.

The second non-Koopmans' state occurs near the third Koopmans' state at about 11 eV. While the lower energy part of the third band system calculated at 11.08 eV may be assigned to the ionization from the $4b_{3g}$ orbital ($^2B_{3g}$ state), the high-energy flank of this band calculated at 11.68 eV is again the second non-Koopmans' state of $^2B_{2g}$. Thus, the present *ab initio* CI results clearly indicate that the two high-energy and low-intensity flanks of the second and third band systems observed in the photoelectron spectrum of PQD can be ascribed to the shake-up ionizations. The present result, therefore, definitely confirms the original assignment of Koenig et al. [4] as for the first non-Koopmans' state in PQD observed at 9.80 eV.

The occurrence of the low lying non-Koopmans' ionizations seems by no means to be confined to PQD. Several unsaturated hydrocarbons exhibited low-lying shake-up bands in the *uv* photoelectron spectra, which were confirmed by semiempirical MO studies [8, 9]. The results obtained from the present *ab initio* CI study are in accord with those of the previous semiempirical MO studies in that two high-energy shoulders observed at 9.8 and 11.0 eV in the photoelectron spectrum of PQD are the non-Koopmans' states. On the other hand, the argument raised by Dewar [7] that these shoulders of the bands are due to the impurity of the

Table 5. Energies of the CI wavefunctions of *p*-quinodimethane[a]

Electronic states	Main excitation	E(CI)	ΔE(CI–SCF)	Dimension	C_0[b]
^1A_g	ground state	−307.64317	−0.18335	2752	0.91248
^1A_g	$(2b_{3u})^2 \rightarrow (2b_{2g})^2$	−307.40823	—	2752	0.89887
$^3B_{1u}(\pi\pi^*)$	$2b_{3u} \rightarrow 2b_{2g}$	−307.55987	−0.15872	4761	0.92911
$^1B_{1u}(\pi\pi^*)$	$2b_{3u} \rightarrow 2b_{2g}$	−307.47705	−0.21825	3168	0.92436
$^3B_{3g}(\pi\pi^*)$	$2b_{3u} \rightarrow 1a_u$	−307.46718	−0.18630	5188	0.89390
$^1B_{3g}(\pi\pi^*)$	$2b_{3u} \rightarrow 1a_u$	−307.43375	−0.17815	3081	0.91940
$^3A_g(\pi\pi^*)$	$2b_{3u} \rightarrow 3b_{3u}$	−307.42744	−0.20381	4927	0.90254
$^3B_{1g}(\sigma\pi^*)$	$4b_{3g} \rightarrow 2b_{2g}$	−307.37140	−0.21503	6525	0.92094
$^1B_{1g}(\sigma\pi^*)$	$4b_{3g} \rightarrow 2b_{2g}$	−307.36631	−0.21608	3768	0.91956
$^3B_{3g}(\pi\pi^*)$	$1b_{1g} \rightarrow 2b_{2g}$	−307.45901	−0.18799	5348	0.88780
$^1B_{3g}(\pi\pi^*)$	$1b_{1g} \rightarrow 2b_{2g}$	−307.40917	−0.18752	3060	0.90418
$^3B_{1u}(\pi\pi^*)$	$1b_{1g} \rightarrow 1a_u$	−307.46362	−0.22583	5202	0.90102
$^1B_{1u}(\pi\pi^*)$	$1b_{1g} \rightarrow 1a_u$	−307.32373	−0.21182	3571	0.89872
$^3B_{2u}(\pi\pi^*)$	$1b_{1g} \rightarrow 3b_{2u}$	−307.32897	−0.18984	5512	0.88035
$^1B_{2u}(\pi\pi^*)$	$1b_{1g} \rightarrow 3b_{2u}$	−307.31491	−0.21478	3960	0.89129
$^3B_{3u}(\pi\sigma^*)$	$2b_{3u} \rightarrow 9a_g$	−307.30972	−0.18461	5668	0.92352
$^1B_{3u}(\pi\sigma^*)$	$2b_{3u} \rightarrow 9a_g$	−307.30460	−0.18403	3229	0.92359
$^3B_{2g}(\pi\sigma^*)$	$2b_{3u} \rightarrow 8b_{1u}$	−307.30363	−0.18263	5568	0.92304
$^1B_{2g}(\pi\sigma^*)$	$2b_{3u} \rightarrow 8b_{1u}$	−307.29259	−0.18135	3227	0.92102

[a] Atomic units. Energy threshold of 5.10^{-5} a.u. has been employed.

[b] Coefficients of the reference configuration

photolysis byproducts, cannot be supported by the present calculation. The HOMO–LUMO excitation of the PQD cation does not lie sufficiently above the Koopmans' configuration in question so as to inhibit the configuration interaction, contrary to the argument raised by Dewar [7].

The energies of the CI wavefunctions for the singlet and triplet excited states of PQD are listed in Table 5. The excited states were determined by the CI calculations based on the open-shell SCF reference configuration for each state of interest. The calculated excited energies for the singlet–singlet and singlet–triplet excitations are summarized in Table 6. The first singlet–singlet excitation is found to be the transition ${}^1B_{1u}(\pi\pi^*) \leftarrow {}^1A_g$, which corresponds to the one-electron $\pi^* \leftarrow \pi$ transition between the HOMO ($2b_{3u}$) and LUMO ($2b_{2g}$). This transition is polarized along the long molecular axis. The calculated transition energy of 4.55 eV with oscillator strength (f) 0.846 may be compared with the experimental value of 4.12 eV reported by Pearson et al. [2]. Only a single and intense *uv* absorption band at 301 mμ (4.12 eV) has been reported experimentally.

The next singlet transitions calculated at 5.70, 6.37 and 7.53 eV are symmetry-forbidden transitions (two ${}^1B_{3g}(\pi\pi^*) \leftarrow {}^1A_g$ and ${}^1B_{1g}(\sigma\pi^*) \leftarrow {}^1A_g$), and there is no experimental result available as yet for these transitions. The next dipole

Table 6. A summary of the caluclated excitation energies and oscillator strengths (f) of p-quinodimethane and comparison with experiment[a]

Electronic states and reference configurations		ΔE(CI)	f[b]	Experiment [2]
Singlet states				
$1A_g$	$(2b_{3u})^2 \rightarrow (2b_{2g})^2$	6.93		
${}^1B_{1u}(\pi\pi^*)$	$(2b_{3u})^1(2b_{2g})^1$	4.55	0.846	4.12
${}^1B_{3g}(\pi\pi^*)$	$(2b_{3u})^1(1a_u)^1$	5.70		
${}^1B_{3g}(\pi\pi^*)$	$(1b_{1g})^1(2b_{2g})^1$	6.37		
${}^1B_{1g}(\sigma\pi^*)$	$(4b_{3g})^1(2b_{2g})^1$	7.53		
${}^1B_{1u}(\pi\pi^*)$	$(1b_{1g})^1(1a_u)^1$	8.69	0.052	
${}^1B_{2u}(\pi\pi^*)$	$(1b_{1g})^1(3b_{3u})^1$	8.93	0.316	
${}^1B_{3u}(\pi\sigma^*)$	$(2b_{3u})^1(9a_g)^1$	9.21		
${}^1B_{2g}(\pi\sigma^*)$	$(2b_{3u})^1(8b_{1u})^1$	9.54		
Triplet states				
${}^3B_{1u}(\pi\pi^*)$	$(2b_{3u})^1(2b_{2g})^1$	2.27		
${}^3B_{3g}(\pi\pi^*)$	$(2b_{3u})^1(1a_u)^1$	4.79		
${}^3B_{1u}(\pi\pi^*)$	$(1b_{1g})^1(1a_u)^1$	4.88		
${}^3B_{3g}(\pi\pi^*)$	$(1b_{1g})^1(2b_{2g})^1$	5.01		
${}^3A_g(\pi\pi^*)$	$(2b_{3u})^1(3b_{3u})^1$	5.87		
${}^3B_{1g}(\sigma\pi^*)$	$(4b_{3g})^1(2b_{2g})^1$	7.39		
${}^3B_{2u}(\pi\pi^*)$	$(1b_{1g})^1(3b_{3u})^1$	8.55		
${}^3B_{3u}(\pi\sigma^*)$	$(2b_{3u})^1(9a_g)^1$	9.07		
${}^3B_{2g}(\pi\sigma^*)$	$(2b_{3u})^1(8b_{1u})^1$	9.24		

[a] Energies in eV.

[b] The oscillator strengths: $f = \frac{2}{3}\Delta E \cdot |t|^2$, where t is the transition moment

allowed transitions occur at 8.69 eV ($f = 0.052$) and 8.93 eV ($f = 0.316$), which are the second $^1B_{1u}(\pi\pi^*) \leftarrow {}^1A_g$ and $^1B_{2u}(\pi\pi^*) \leftarrow {}^1A_g$ transitions.

The lowest lying triplet state, which corresponds also the HOMO–LUMO excitation, $^3B_{1u}(\pi\pi^*) \leftarrow {}^1A_g$ is calculated at 2.27 eV.

There are some previous semiempirical MO calculations available for the interpretation of the electronically excited states of PQD and its derivatives [6, 10, 12, 13]. A detailed MO treatment of a series of *p*-quinodimethane molecules had been carried out as early as 1951 by Pullman et al. [6]. A semiempirical π-electron calculation for three isomeric quinodimethanes was also reported by Flynn and Michl [12]. Most recently, Åsbrink et al. [13] studied the electronic spectrum of tetracyano-quinodimethane by the semiempirical HAM/3 method, and finally Bigelow [10] investigated the electronic structure and spectrum of PQD by the CNDO/S and INDO methods. The calculated singlet–singlet transition energies obtained by the CNDO/S-CI study for the quinoid structure of PQD [10] are in accord with the present *ab initio* CI results. However, the lowest triplet state calculated at 1.05 or 1.72 eV seems to be too low comparing with the present value of 2.27 eV. The triplet manifold of the $\pi\pi^*$ excited states in PQD is almost unexplored in the experimental study.

As a reference for the future studies, some calculated molecular properties of PQD are listed in Table 7. They include the net charges, overlap populations

Table 7. Some molecular properties of *p*-quinodimethane, calculated using the CI wavefunctions

	Ground state (^1A_g)	Lowest triplet state $^3B_{1u}(\pi\pi^*)$	Lowest singlet state $^1B_{1u}(\pi\pi^*)$
Net charges			
C(C=C)	−0.263	−0.266	−0.255
C(>C=)	−0.015	−0.023	0.0
C(=CH$_2$)	−0.529	−0.498	−0.558
H(ring)	+0.280	+0.274	+0.278
H(CH$_2$)	+0.255	+0.253	+0.256
Overlap populations			
C=C	1.222	1.090	1.128
C—C	0.865	1.008	0.926
>C=CH$_2$	1.188	0.894	1.022
C—H(ring)	0.738	0.739	0.731
C—H(CH$_2$)	0.744	0.746	0.737
Second moments[a]			
$\langle x^2 \rangle$	−34.191	−34.601	−37.380
$\langle y^2 \rangle$	−31.779	−31.475	−31.403
$\langle z^2 \rangle$	−41.127	−41.015	−41.961
$\langle r^2 \rangle$	−107.097	−107.091	−110.744

[a] Calculated at the center of mass in a.u. The molecule lies in the *xz*-plane, the *z* axis being the longer axis

and the second moments for the ground and electronically excited first singlet and triplet states.

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