Finally, we turn to a common unjustified custom that springs from resort to the RRK classical treatment. Even though a fall-off curve has been well matched by some RRK curve, with ν and b determined from an Arrhenius plot of the high-pressure rate constants, the calculated $B(E)$, average energy and most importantly, k_E, will usually differ greatly from those of the real molecules and from the k_E values given by RRKM or other more realistic treatment. The custom of estimating k_E values for nonthermal systems by use of the Kassel eq 4, with insertion of the relevant E values and with employment of s values deduced from thermal data, invites catastrophe. Thus, in the cis-butene case at $1300°K$, for some arbitrary energy, say 90 kcal mol^{-1}, as might arise in a chemical activation or photon activation system, Figures 3 and 4 show that the calculated k_E values ($x \simeq 10$) are $\sim 10^6$ sec^{-1} (RRKM) and $\sim 10^2$ sec^{-1} (RRK, $s = 22$). The "correct" $s(k_E)$ in this instance is $s \simeq 17$; thus a better estimate from thermal data of the correct s for use in the classical Kassel k_E expression is found as $s(k_E) \simeq \frac{1}{2}[s(C_{vib}) + s(E_{vib})]$. Of course, $s(k_E)$ is not a fixed value; in the case of cis-2-butene at $1300°K$, it rises to $s = 19$ for $x = 30$ and drops to $s = 13$ for $x = 5$; also, the correct $s(k_E)$ at given x also depends on temperature.

CNDO–CI Studies of the Effects of Multiple Substitution on the

Electronic Spectrum of p-Benzoquinone

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The CNDO–CI method of Del Bene and Jaffé has been used to calculate the uv spectra of p-benzoquinone and all its methyl derivatives. The uv-visible absorption spectrum of p-benzoquinone is qualitatively well represented, although the two $\pi-\pi^*$ transitions are calculated to be about 8 kK higher than observed. The calculated orbital energies agree reasonably well with the photoelectron spectrum. The substituent induced changes in the uv spectrum are quite well reproduced by the calculation, but there seems to be no simple way to relate the parameters of this MO approach to the parameters used in the phenomenological description of substituent effects.

Introduction

The relationship between the uv spectra of derivatives of p-benzoquinone (PBQ) and the structure of these derivatives has been studied by a perturbation theory approach.[1-4] The observed spectrum of PBQ was taken as the solution to the unperturbed problem, and the substituents were represented as perturbations to the excited states. The formalism of the second-order perturbation equations[5] divides the substituent effect into two kinds: a conjugative (or mesomeric[6]) effect where excited states of the substituents mix with the excited states of the PBQ; and an inductive effect where the substituents cause the PBQ states to mix with each other. The conjugative effect depends only on the numbers and types of substituents, while the inductive effect depends on the relative positions of substitution as well as on the numbers and types of substituents. Simple formulas for frequency and intensity shifts of the two $\pi-\pi^*$ transitions in PBQ and its derivatives were derived, and inductive and conjugative parameters for a number of substituents were obtained from spectra.[2] Spectra of other derivatives were successfully predicted from the parametrized formulas.

The perturbation approach works well only for weak substituents such as CH_3 and Cl and breaks down for strong substituents such as NH_2 and NO_2 which substantially expand the π system. However, the strong substituents can, in principle, be treated by the Pariser–

(1) L. E. Orgel, *Trans. Faraday Soc.*, **52**, 1172 (1956).

(2) P. E. Stevenson, *J. Mol. Spectrosc.*, **17**, 58 (1965).

(3) P. E. Stevenson, *J. Chem. Phys.*, **43**, S27 (1965).

(4) P. E. Stevenson, *J. Mol. Spectrosc.*, **23**, 191 (1967).

(5) J. Petruska, *J. Chem. Phys.*, **34**, 1111 (1961).

(6) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 211.

Parr–Pople method.[7] For CH$_3$ though, it is difficult to define and parametrize an addition to the π system of a parent compound. Moreover it is likely that a substituent perturbs both the σ and π systems of the parent compound. Finally it is now possible to perform calculations which take into account all the valence electrons in a molecule, both σ and π.[8]

The work described in this paper consists of calculations on PBQ and all six of its methyl derivatives with the intent of predicting the electronic spectrum of each of the seven compounds. The modified CNDO method of Del Bene and Jaffé with configuration interaction was chosen for these calculations.[9] This method has been used successfully to predict the spectra of a number of aromatic compounds and some of their monosubstituted derivatives, as well as some small molecules. The formulas and parametrization employed in this study are given in the original references except that the two-electron, two-center integrals were calculated by the Mataga approximation[10] instead of the Pariser formula.[11] It was hoped that this work would show the relationship between the orbital and perturbation approaches to prediction of electronic spectra, but it will be seen below that this hope has only been realized in part.

Details of the Calculations

The MO–CI calculations were performed with the program CNDO/S–CI.[12] Coordinates for PBQ were obtained from the work of Robertson.[13] Methyl groups were assumed to have the geometry shown in Figure 1. The methyl carbon was assumed to have tetrahedral geometry. The angles of the C–C bond with the ring were assumed to be the same as those of the C–H bond in PBQ. Cartesian coordinates were calculated with the time-sharing version of COORD.[14] The number of configurations taken for CI was in each case equal to the number of orbitals, or 36 plus 6 for each methyl group.

The Spectrum of p-Benzoquinone

The electronic spectrum of PBQ (Figure 2) is well known[15] and consists of three absorption bands in the visible and near-uv. The lowest energy band ($\nu = 20$–25 kK, $\epsilon = 20$, $f = 0.0004$) arises from n–π^* absorption and is labeled ^1A–^1U in the Platt notation. The other two bands ($\nu = 36$ kK, $\epsilon = 300$, $f = 0.0008$; and $\nu = 41$ kK, $\epsilon = 20,000$, $f = 0.4$) arise from π–π^* transitions. The assignment of these two transitions, based on substituent perturbations, are $^1A_{1g}$–$^1B_{1g}$ and $^1A_{1g}$–$^1B_{3u}$, respectively.[1] For the purpose of discussing the spectra of derivatives of PBQ where the symmetry is lower, an alternate notation has been proposed which labels the two transitions as ^1A–^1K and ^1A–^1J, respectively.[2]

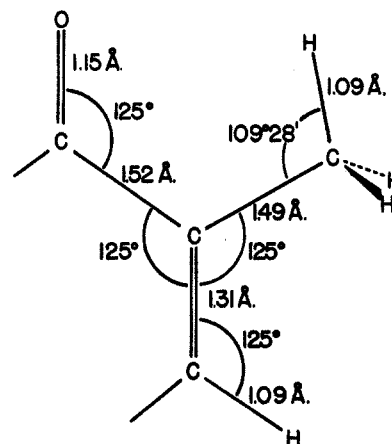The CNDO–CI calculation (Table I) reproduces the observed spectrum of PBQ quite well except that the

Figure 1. Geometry of methyl-p-benzoquinone used in calculations.

^1A–^1J and ^1A–^1K transition energies are overestimated by about 8 kK (1 eV). The n–π^* absorption is predicted to occur right where it is observed. Moreover, the calculation shows that this absorption arises from two transitions, there being two oxygen lone-pair orbitals from which n–π^* transitions can arise. A third n–π^* transition (^1A_g–$^1B_{1u}$) is calculated to occur at 40.8 kK, below the first calculated π–π^*. However, one would not expect to observe it, since its calculated energy is greater than that of the observed ^1A–^1K transition (^1A_g–$^1B_{3g}$) which has considerably more intensity than would be expected from n–π^* absorption.

Table I: The Electronic Spectrum of p-Benzoquinone

Transition	Symmetry	ν^a Obsd	ν^a Calcd	f^b Obsd	f^b Calcd
^1A–^1U	^1A_g–$^1B_{3g}$	22	21.1	0	0
	^1A_g–^1A_u		23.6		0
^1A–^1K	^1A_g–$^1B_{1g}$	36.2	44.3	0	0
^1A–^1J	^1A_g–$^1B_{3u}$	41.7	49.2	0.4	0.64

^{a} Energies in kK. ^{b} Electronic component of oscillator strength.

(7) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1963.

(8) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); (c) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(9) J. Del Bene and H. H. Jaffé, *ibid.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 1126 (1969).

(10) K. Nishimoto and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957); **13**, 140 (1957).

(11) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

(12) J. Del Bene, H. H. Jaffé, R. L. Ellis, and G. Kuehnlenz, CNDO-S/CI, program no. 174, Quantum Chemistry Program Exchange, Indiana University (1971).

(13) J. M. Robertson, *Proc. Roy. Soc., Ser. A*, **150**, 106 (1935).

(14) P. E. Stevenson and J. E. Merrill, COORD, program no. 186, Quantum Chemistry Program Exchange, Indiana University (1971).

(15) W. Flaig, Th. Ploetz, and A. Küllmer, *Z. Naturforsch. B*, **10**, 668 (1955).
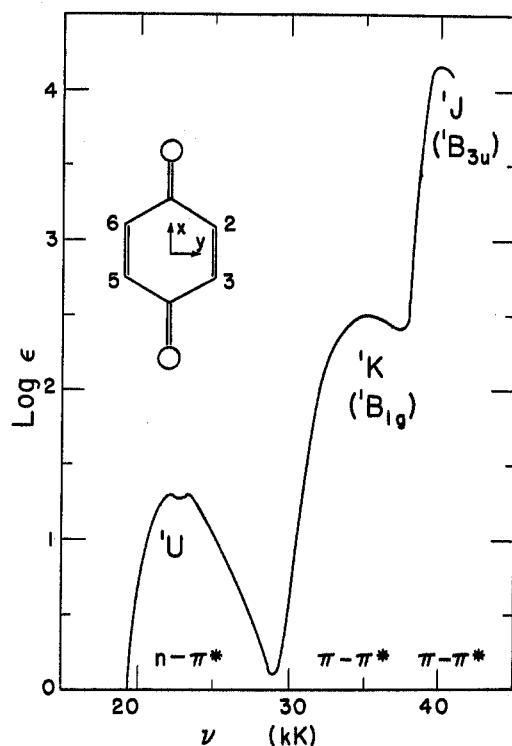
Figure 2. Electronic spectrum of p-benzoquinone (from ref 15.). The two bumps in the ^1U peak are calculated in this work to arise from two n–π^* transitions (into $^1B_{3g}$ and ^1A_u states).

A prediction of the photoelectron spectrum of PBQ may be made from this calculation. Peaks in photoelectron spectra correspond to vertical ionizations which in turn correspond to calculated molecular orbital energies according to Koopmanns' theorem. The photoelectron spectra of PBQ and its tetrafluoro derivative have been discussed by Brundle, Robin, and Kuebler.[16] Making use of the "perfluoro effect" which stabilizes σ orbitals by $ca.$ 5 eV in perfluoro compounds with respect to the unsubstituted parents (π orbitals are stabilized hardly at all), they assigned the ionizations at 10.11 and 11.5 eV to n orbitals, the ionizations at 10.41 and 11.06 eV to π orbitals, and the ionization at 13.43 eV to a σ orbital. These assignments are shown in Table II along with assignments made by this author of several other peaks in their spectrum and the corresponding calculated orbital energies. Agreement of the orbital energies with the observed ionizations is quite good. The observed large gap between the fourth and fifth ionization potentials is reproduced (albeit exaggerated) by the calculation; only the position of the $b_{2u}(n)$ orbital is out of the observed order; and most of the energies agree within a root mean square deviation of ± 0.5 eV. (All agree within ± 1.0 eV.)

Effects of Methyl Substitution

The results of calculations on the methyl derivatives of PBQ are shown in Table III and Figures 3 and 4.

Table II: Molecular Orbitals of p-Benzoquinone

Calculated orbitals		Observed photoelectron spectrum[b]	
Energy, eV	Symmetry[a]	Energy, eV	Assignment
−9.92	b_{1g} (n)	10.11	n_g
−10.91	b_{1u} (π)	10.41	π
−11.03	b_{3g} (π)	11.06	π
−10.61	b_{2u} (n)	11.5	n_u
−14.31	a_g (σ)	13.43	σ
−14.98	b_{1g} (σ)	14.3[c]	σ
−15.05	b_{2g} (π)	14.7[c]	π
−15.42	b_{3u} (σ)	15.2[c]	σ
−16.11	b_{2u} (σ)	16.1[c]	σ
−16.36	b_{1u} (π)	16.6[c]	π

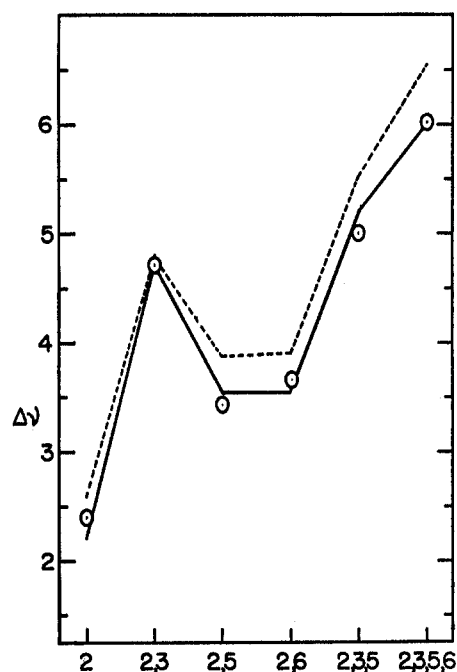[a] Axes as shown in Figure 2. [b] Reference 16. [c] Energy read from curve in Figure 7, ref 16.

Figure 3. Frequency shifts of the ^1A–^1K transition in the methyl PBQ's: CNDO–CI calculation (- - -); perturbation treatment (——); observed (⊙).

The observed changes in transition energies and electronic oscillator strengths in the ^1A–^1K and ^1A–^1J transitions are qualitatively well represented. In particular the calculations predict quite well the way the spectrum of the 2,3 derivative differs from those of the 2,5 and 2,6 derivatives. Quantitative accuracy is not quite as good. The frequency shifts of the ^1A–^1K and ^1A–^1J transitions are overestimated by about 8 and 50%, respectively, and the substituent induced electronic oscillator strengths of the ^1A–^1K transition

(16) C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **94**, 1466 (1972).

Table III: Effects of Methyl Substitution on the Spectrum of p-Benzoquinone

		Methyl groups at positions					
		2	2,3	2,5	2,6	2,3,5	2,3,5,6
				$^1A-^1K$			
$\Delta\nu^a$	Calcd[b]	2.58	4.78	3.87	3.91	5.52	6.54
	Perturbation[c]	2.20	4.72	3.54	3.54	5.20	6.00
	Obsd[d]	2.41	4.72	3.44	3.66	5.00	6.02
f^e	Calcd	0.048	0.088	0	0.0022	0.020	0
	Perturbation	0.0048	0.019	0	0	0.0048	0
	Obsd	0.0070	0.018	0	0.0012	0.0039	0
				$^1A-^1J$			
$\Delta\nu$	Calcd	0.81	1.34	2.48	2.62	3.25	4.29
	Perturbation	0.68	0.92	1.56	1.56	2.06	2.76
	Obsd	0.69	1.02	1.51	1.67	1.99	2.76
f	Calcd	0.52	0.34	0.58	0.58	0.50	0.54
	Obsd	0.5	0.3	0.4	0.4	0.4	0.4

[a] Frequency shifts (in kK) relative to transition frequency in PBQ. [b] This work. [c] Reference 2. [d] Reference 15. Spectra observed in n-C_6H_{14}. [e] Electronic component of oscillator strength.
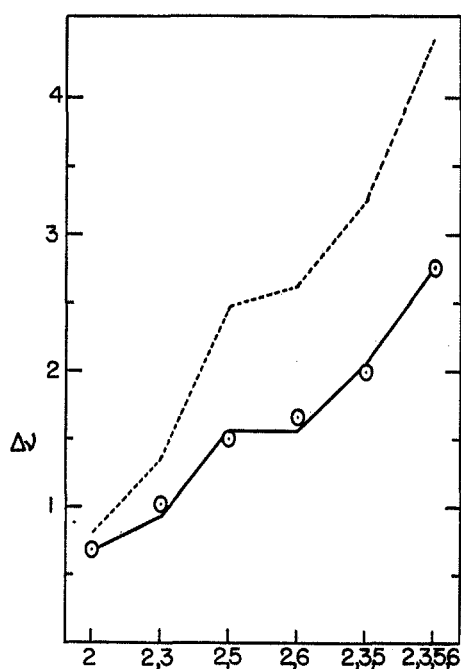

Figure 4. Frequency shifts of the $^1A-^1J$ transition in the methyl PBQ's: CNDO-Cl calculation (– – –); perturbation treatment (——); observed (⊙).

are overestimated by a factor of 5. The predicted shifts in the energies of the two low-lying n–π* transitions are all quite small, agreeing with the observation that the $^1A-^1U$ band is little affected by substitution.[2]

Discussion

It is evident from the above calculations that the modified CNDO method with CI[9] is successful in accounting for the effects of substitution on the electronic spectrum of PBQ. Although the quantitative results are not as good as might be desired, the calculations closely parallel the observed effects of methyl substitu-

tion. This is especially true of the three isomers of dimethyl PBQ where the relative positions of the substituents govern the changes in the spectra. There is a considerably greater red shift and much more intensity in the $^1A-^1K$ transition of 2,3-dimethyl PBQ than in the $^1A-^1K$ transitions of the 2,5 and 2,6 isomers, and these differences are rather well predicted by the calculations.

However, in spite of the parallel results of the perturbation method and the molecular orbital method, there seems to be no simple way to identify anything at any stage in the MO procedure as either an inductive or conjugative perturbation. An analysis of the π matrix elements of the Hamiltonians of all seven compounds showed only very small and unsystematic variations among corresponding elements. Average values of these elements with r.m.s. deviations are given in Table IV. The only substituent caused perturbation to the MO Hamiltonian is its enlargement to accommodate the substituent atomic orbitals.

Table IV: π Matrix Elements from the CNDO Hamiltonians of Methyl-Substituted p-Benzoquinones (in eV)

Diagonal elements			Off-diagonal elements		
Atom	Position	Value	Bond	Position	Value
C	1	-5.58 ± 0.10	C—C	1-2	-2.54 ± 0.02
C	2	-5.89 ± 0.07	C=C	2-3	-5.41 ± 0.03
O	7	-8.69 ± 0.08	C=O	1-7	-7.29 ± 0.01
C	(CH₃)	-5.70 ± 0.03	C—C	(CH₃)	-2.46 ± 0.01
H	(CH₃)	-7.34 ± 0.03	C—H	(CH₃)	-7.97 ± 0.001

This is not to say that the MO's are not perturbed. In fact the MO's undergo considerable change when methyl groups are introduced. There are some energy

Table V: Calculated Spectra of the Methyl PBQ's—Comparison of Single Configuration Results with Full CI Treatment

		PBQ	2	2,3	2,5	2,6	2,3,5	2,3,5,6
				^1A–^1K Transition				
Single configuration	Energy[a]	45.69	44.57	41.59	41.56	41.49	40.82	38.76
	Shift[b]	...	1.12	4.10	4.13	4.19	4.87	6.83
	f^c	0	0.54	0.44	0.0002	0.0020	0.29	0
CI	Energy[a]	44.28	41.70	39.50	40.41	40.37	38.76	37.74
	Shift[b]	...	2.58	4.78	3.87	3.91	5.52	6.54
	f^c	0	0.049	0.088	0	0.0022	0.020	6.54
Observed[d]	Shift[e]	...	2.41	4.72	3.44	3.66	5.00	6.02
	f^c	0	0.0070	0.018	0	0.0012	0.0039	0
				^1A–^1J Transition				
Single configuration	Energy[a]	51.16	48.78	49.43	49.20	48.34	46.78	46.57
	Shift[b]	...	2.38	1.73	1.96	2.82	4.38	4.59
	f^c	1.34	0.67	0.75	1.23	1.22	0.87	1.18
CI	Energy[a]	49.19	48.38	47.86	46.72	46.58	45.94	44.90
	Shift[b]	...	0.81	1.34	2.48	2.62	3.25	4.29
	f^c	0.64	0.53	0.34	0.58	0.58	0.51	0.54
Observed[d]	Shift[e]	...	0.69	1.02	1.51	1.67	1.99	2.76
	f	0.4	0.5	0.3	0.4	0.4	0.4	0.4

[a] Calculated energies in kK. [b] Shift of energy relative to equivalent stage of PBQ calculation. [c] Electronic component of oscillator strength. [d] Reference 15. Spectra observed in n-C_6H_{14}. [e] Shift of transition frequency relative to observed PBQ spectrum.

Table VI: Fraction of Charge Found on the CH_3 Groups in the Spectroscopically Important π-MO's

Orbital		PBQ	2	2,3	2,5	2,6	2,3,5	2,3,5,6
ψ_{-3}	ϵ^a	0.973	1.039	1.081	1.097	1.088	1.135	1.174
	q_{CH_3}[b]	...	0.00	0.00	0.00	0.00	0.00	0.00
ψ_{-2}	ϵ	−0.257	−0.179	−0.107	−0.097	−0.101	−0.030	0.034
	q_{CH_3}	...	0.01	0.02	0.02	0.02	0.02	0.03
ψ_{-1}[c]	ϵ	−1.788	−1.715	−1.649	−1.628	−1.642	−1.570	−1.506
	q_{CH_3}	...	0.01	0.01	0.01	0.01	0.02	0.02
ψ_1[d]	ϵ	−10.909	−10.426	−10.019	−10.318	−10.318	−9.951	−9.815
	q_{CH_3}	...	0.08	0.10	0.09	0.09	0.14	0.13
ψ_2	ϵ_3	−11.030	−10.913	−10.817	−10.431	−10.420	−10.352	−10.057
	q_{CH_3}	...	0.00	0.00	0.06	0.06	0.07	0.10

[a] Orbital energies in eV. [b] Fraction of charge summed over all CH_3 groups. [c] Lowest empty MO. [d] Highest occupied MO.

shifts, of course, but the most notable change is a fairly thorough mixing of the b_{1u} and b_{3g} MO's (the two highest occupied MO's) of PBQ in all the derivatives except tetramethyl PBQ, brought about by the reduction from D_{2h} symmetry.

The fact that the π Hamiltonian elements are nearly invariant from one methyl-substituted PBQ to the next might tempt one to try predicting spectra by use of these elements in a Hückel MO calculation. However, one would still need to compute the two electron integrals necessary for calculation of the energies of excited configurations. Moreover, the energies of the excited configurations of PBQ derivatives do not give good predictions of substituent effects; so one would need to perform a CI calculation as well. In particular, the energies of the lowest excited π–π configurations of the three dimethyl derivatives are nearly identical

(see Table V). It is only when configuration interaction is included that the CNDO method gives its good account of the effects of methyl substituents.

The origins of the inductive and conjugative effects may be qualitatively accounted for by the CNDO-CI calculations. Table VI indicates that the highest two occupied π orbitals are spread out appreciably onto the CH_3 groups of the substituted PBQ's whereas the lowest three empty π MO's are almost completely confined to the ring. Thus there is a significant charge transfer from CH_3 to ring when an electron undergoes a π–π^* excitation. (There follows some amount of rearranging of the charge transfer upon CI mixing.) The CI, however, does not bring about any additional charge transfer, as the configurations which would bring this about are of such high energy as to be of no importance. Thus the conjugative effect

seems to appear on the MO level. On the other hand, the CI seems to contain most of the inductive effect, the clearest evidence for this being the calculations of the three dimethyl isomers (Table V). In the perturbation model, the 2,3 isomer has the largest inductive effect of all the derivatives, while in the 2,5 and 2,6 isomers there is none. Since the CI step is necessary to match these results, the CI must account for much of the inductive effect.

Quantitatively, however, it does not seem possible to relate the inductive and conjugative parameters to such quantities as orbital energies, single configuration energies, CI matrix elements, or CI mixing coefficients. This would be possible if the single configurations corresponded to the unperturbed ring and substituent states of the perturbation method, and if the configurations were essentially the same for all the compounds (as are the ring states in the perturbation treatment). However, since the single configurations are built of MO's and since many of the MO's are different from one compound to the next, the single configurations of one derivative are different from those of the next, and comparison of, say, CI matrix elements for the two derivatives becomes meaningless in terms of calculating perturbation parameters.

Further evidence for the above claim comes from examination of the calculated shifts in energy between PBQ and its methyl derivatives. If the conjugative effect were described entirely by the single configuration energies, and if the inductive effect were described entirely by CI, the configuration energy shifts would be proportional to the number of CH_3 groups. Moreover, the CI would cause additional shifts only for the 2, 2,3, and 2,3,5 derivatives.[2] Table V shows that this is obviously not the case. Thus the inductive and conjugative effects must both contribute to changes in MO's, excitation, and CI, and there seems to be no simple way to calculate values for the inductive and conjugative parameters from intermediate quantities obtained from the CNDO-CI calculation.

Summary

Introduction of a substituent into the CNDO-CI framework produces (1) an expansion of the Hamiltonian but no important changes in the values of the matrix elements; (2) changes in MO's, MO energies, and configuration energies, and (3) changes in the extent of interaction among configurations; proper account of substituent effects occurs only upon CI. Introduction of a substituent into the perturbation framework produces (1) mixing of the states originally present in the parent compound as measured by the inductive parameter, and (2) mixing of substituent states with parent states as measured by the conjugative parameter. There seems to be no simple way to associate the individual steps of one method with those of the other. Thus there is no direct way of calculating inductive and conjugative parameters within the CNDO-CI method.

Proponents of the perturbation method of handling the effects of substituents on electronic spectra made the point long ago that one should think in terms of electronic states in discussing spectra rather than in terms of molecular orbitals.[17] These calculations reinforce this point. Good account of the substituent effects here is not obtained at either the orbital stage or even the single configuration stage, but only when states have been constructed through configuration interaction.

(17) J. R. Platt, personal communication.