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MO Theoretical Studies on Stereoelectronic Control in the Addition Reaction of 1, 4-Benzoquinone-4-(O-methyloxime)[*]

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The chlorine addition and Diels–Alder cycloaddition of cyclopentadiene to 1, 4-benzoquinone-4-(O-methyloxime) have been studied MO theoretically. It has been shown that the reactions occur predominantly to the quinone ring double bond which is oriented anti to the nitrogen lone pair due to an n–σ^* interaction between the nitrogen lone pair, n, and the app. vicinal bond, causing the π bond to be weakened and destabilized due to the less conjugation from reduced delocalization.

Structure-reactivity relation has been a subject of great interest in organic chemistry. In the kinetic controlled chlorine addition and Diels–Alder cycloaddition of cyclopentadiene (CPD) to 1, 4-benzoquinone-4-(O-methyloxime) (1), the overwhelming predominance of products which have the configuration (2) where the oxime group is anti to the remaining double bond was found over the alternative arrangement (3). The NMR studies of Baldwin and Norris have shown 70 % and 90 % of anti products in the two addition reactions respectively.[1]

TABLE 1: Energy Components (a.u.) (Relative Values are in kcal/mole)

Energy	Ia	Ib
E_{TOT}	−103.2438	−103.3720
ΔE_{TOT}	80.5	0.0
$\Delta 2\sum_{i}^{\infty}\varepsilon_i$	0.0	281.9
$\Delta(V_{nn}-V_{ee})$	362.4	0.0

In this work we report results of an MO theoretical investigation on a difference in chemical reactivity of the two quinonoid double bonds focussing our attention on the effect of orientation of nitrogen lone pairs. Since we are prima-

TABLE 2: Eigenvector and π Bond Order of 1,4-Benzoquinone-4-(O-methyloxime)

| HOMO						LUMO				π bond order	
C_2	C_3	C_5	C_6	Energy	C_2	C_3	C_5	C_6	Energy	P_{23}^π	P_{56}^π
0.3547	0.2507	0.2074	0.2852	−0.4282	0.4993	−0.5056	0.4700	−0.4972	0.1678	0.9036	0.9398
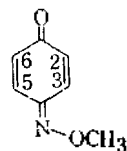
rily concerned with orbital properties, the semi-empirical MO method of CNDO/2[2] has been employed in this work.

Calculations

All calculations were carried out using CNDO/2 program. Bond lengths and bond angles adopted were the standard values.[3]

Results and Discussion

Two possible conformers (1a) and (1b) are considered in order to determine the stable form.

(1a)   (1b)
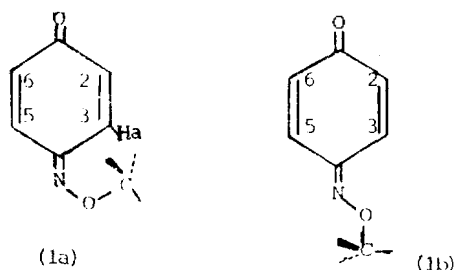
At the outset, simple application of the π-NBI method[1] readily predicts the (1b) form to be the preferred one, since there is a stabilizing $(5\pi/4)$[4] structure in (1b) which is converted to a destabilizing $(7\pi/6)$ structure in (1a) as a result of rotation about N-O single bond. This prediction is confirmed with the computational results in Table 1.

As expected the steric factor is predominant in determining the conformational preference; in (1a) form steric repulsion between methyl hydrogens and ring hydrogen (H_a) is expected as a result of their close approach. Although the total one-electron factor appears to favor (1a) over (1b), it is mainly due to the $n-\sigma^*$ interaction of oxygen lone pairs (n) with the σ^* orbital of the vicinal C-N bond which are oriented antiperiplanar (app) to the n lobe.

Since the chlorine addition to (1) occurs by cleaving π bond C=C, of quinone, the reactivity will be greater, the smaller the π bond order is. Reference to Table 2 indicates that π bond order between C_2 and C_3 atoms, P_{23}^π, are smaller than that between C_5 and C_6 atoms, P_{56}^π; hence on account of π bond order we would expect the addition to occur more readily on $C_2=C_3$ rather than on $C_5=C_6$.

It has been shown that among the four principal intermolecular interaction terms, electrostatic, polarization, exchange repulsion and charge transfer,[5] the charge transfer energy term is the most important one in determining Diels-Alder reactivity.[6,7] Since in the cycloaddition reaction of cyclopentadiene with (1), the latter reacts as a dienophile, the activity *i.e.*, the magnitude of AO coefficients, of carbons
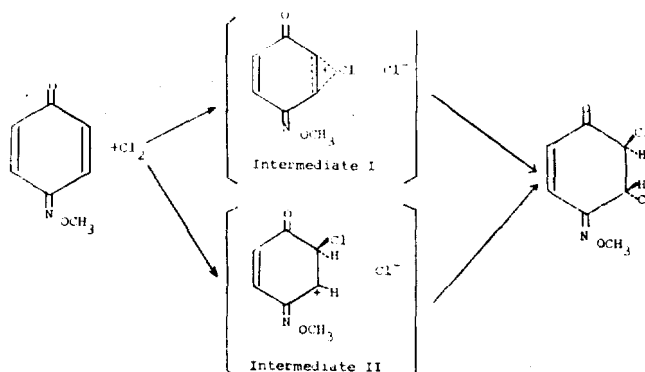

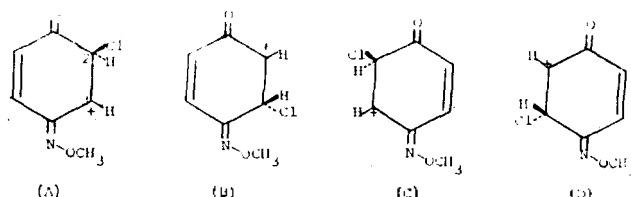Figure 1. Intermediate in chlorine addition reaction

(A)   (B)   (C)   (D)

Figure 2. Structure of intermediate II.

TABLE 3: Energies of Intermediates

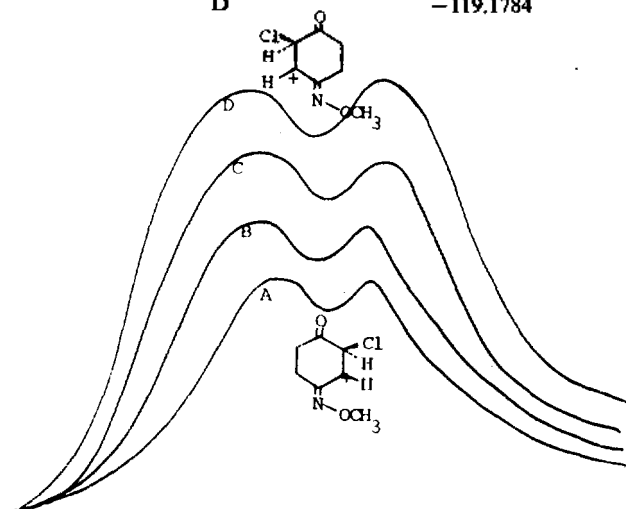| Intermediate form		Energy (a. u.)
Anti	A	−119.2641
	B	−119.2489
Syn	C	−119.1970
	D	−119.1784

Figure 3. Schematic presentation of reaction coordinates.

forming double bonds in the quinone ring are of utmost importance. We have compared the AO coefficients of highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the four quinone ring carbons in Table 2. The AO coefficients of C_2 and C_3 are numerically greater than those of C_5 and C_6 for both frontier orbitals (FMO),[7] indicating that $C_2=C_3$ bond will react preferably in the Diels-Alder cycloaddition.

Chlorine Addition

In the chlorine addition reaction to a double bond of quinone, two intermediates are conceivable: a chloronium ion type intermediate I and a carbonium ion type II. In the former (I) however a bridging group formation is involved, which is a difficult process in chlorination.[8]

Thus we will only consider the type II intermediate. Four possible structures of type II intermediate, A, B, C, and D, have been treated MO theoretically and results are summarized in Table 3.

Of the four, the two, A and B, have the unreacted double bond anti to the methyloxime group, while the other two, C and D, have the syn configuration. It is quite reasonable to assume that the stability of the intermediate determines the reactivity of chlorine addition reaction, since the reaction has shown to be a kinetically controlled type, Figure 3.

Comparison of energies in Table 3 shows that in general anti types are preferred and the intermediate A is the most stable. Chlorine addition to (1) should, therefore, be a two step reaction; after the rate determining addition of Cl^+ to a carbon forming a carbonium ion, Cl^- ion then reacts with the carbonium ion in a fast step. The rate determining addition of Cl^+ can occur either on C_2 or C_6 atom. The C_2 atom is preferred since the electron density of C_2 (1.0253) is greater than that of C_6(0.9747). Thus the products will be predominantly the anti type as experimentally found.

Diels–Alder Cycloaddition

Diels–Alder cycloaddition of (1) to cyclopentadiene (CPD) is known to give three adducts shown in scheme 1.

Scheme I
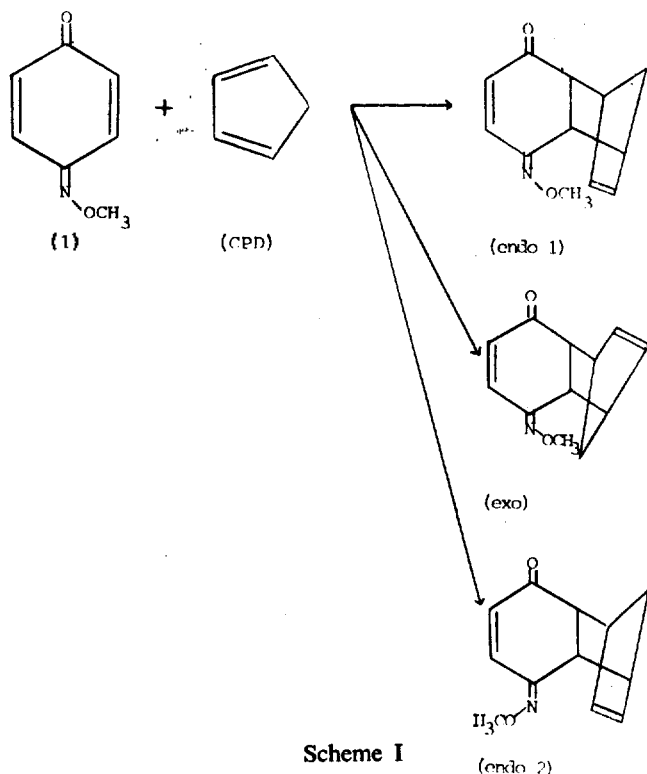
Since the HOMO-LUMO energy gaps between cyclopentadiene (CPD) and, (1) are approximately the same, *i. e.*, ΔE $= E^{LU}_{CPD} - E^{HO}_{(1)} = E^{LU}_{(1)} - E^{HO}_{CPD}$, interaction energies between diene
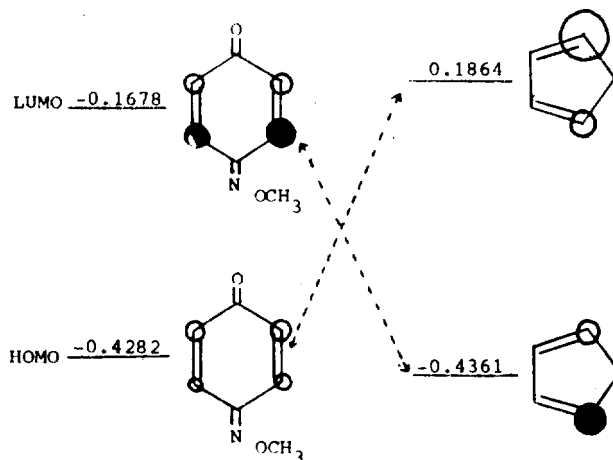

Figure 4. Interactions between HOMO's and LUMO's of diene and dienophile
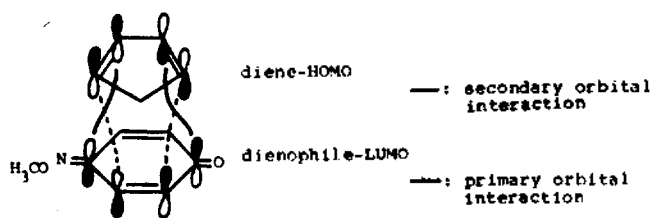

Figure 5. Orbital Interactions in Diels-Alder reaction between (1) and CPD.

—— : secondary orbital interaction

.... : primary orbital interaction

TABLE 4: Comparison of Stabilization Energies Calculated by various Approximation Method (kcal/mol) and Relative Experimental Yield

	4–C	2–C	S.O.I	Expt.
endo 1	50.4	29.9	56.2	90%
exo	49.3	25.8	55.1	8%
endo 2	43.7	25.0	48.7	2%

(CPD)-HOMO and dienophile (1)-LUMO and between diene-LUMO and dienophile-HOMO will contribute about equally to the charge transfer stabilization energy. The reaction can be classified as a neutral electron demand type.[9]

Three approximate methods of estimating the stabilization energy, 4-center (4-C),[9,10] 2-center (2-C)[9,11] and secondary orbital interaction (S.O.I) methods,[9,12] have been applied to the three adducts formation.

The results shown in Table 4 clearly indicate preference of endo 1 type formation in agreement with experimental result. Qualitatively the relative yield of various adducts agrees with our results of stability order.

In a neutral electron demand type reaction, matrix element, H, which is determined by the FMO-AO coefficients is more important for stabilization[13] $\left(S. E \ \alpha \dfrac{H^2}{\Delta E}\right)$ of primary products than the energy gap, ΔE. In the Diels-Alder cycloaddition of (1) with cyclopentadiene, the endo form is favored over the exo due to activation of FMO-AO coefficients; the diene-HOMO and dienophile-LUMO as well as diene-LUMO and dienophile-HOMO are polarized in the same

TABLE 5. Comparison of π Overlap Population

p_{ij}^{x}	(1)	(3)	$\Delta p^x(3)$	p_{ij}^{x}	(1)	(2)	$\Delta p^x(2)$
p_{56}^{x}	0.0682	0.0670	−0.0012	p_{45}^{x}	0.0682	0.0671	−0.0011
p_{23}^{x}	0.2439	0.2451	+0.0012	p_{56}^{x}	0.2458	0.2452	−0.0006
p_{47}^{x}	0.2224	0.2478	+0.0254	p_{47}^{x}	0.2224	0.2272	+0.0048

direction. The endo 1 is formed predominantly over the endo 2 form, simply because of larger magnitudes of FMO–AO coefficients for C_2 and C_3 atoms compared with those for C_5 and C_6 atoms of dienophile. Thus the Diels–Alder reactivity as well as the chlorine addition reactivity are greater for the double bond which is oriented anti to the methyloxime group.

Let us now examine MO theoretically the cause of this reactivity difference.

(2)   (3)
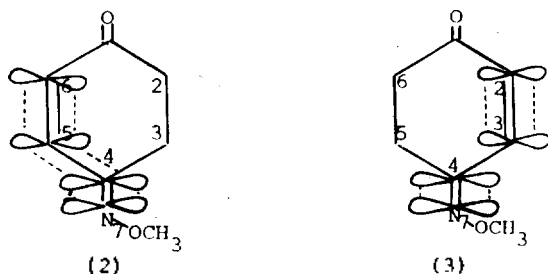
It has been shown that the interaction of nonbonded electron (n) with vicinal σ^* antibonding orbitals is especially efficient and stabilizing, when they are oriented in an antiperiplanar (app) (or in a trans) fashion.[13] As a result of this n-σ^* interaction, the vicinal bonds which are app. to n lobes are weakened and hence lengthened. Thus in structure (3) the app. bond to the nitrogen lone pair i. e., C_3-C_4 bond, is weakened and π overlap population of C_3-C_4 bond decreases, causing π electrons to become somewhat localized on $C_2=C_3$ and $C_4=N_7$ bonds. This reduces in turn the delocalization of lone pair on oxime oxygen atom. Comparison of changes. ΔP_{ij}^x (X)= P_{ij}^x (X)−P_{ij}^x (1) where (X) denotes the adduct x, in π overlap populations summarized in Table 5 clearly shows the more localized nature of double bonds, $C_2=C_3$ and $C_4=N_7$ in (3) as compared with the relatively delocalized nature of $C_5=C_6$ and $C_4=N_7$ in (2).

Since (2) has the more delocalized structre, it will be more stabilized, consequently, compared to (3).

This is clearly supported by the relative stability of two products formed from chlorination of (1), i. e., (2') and (3') below.

(2)   (3)
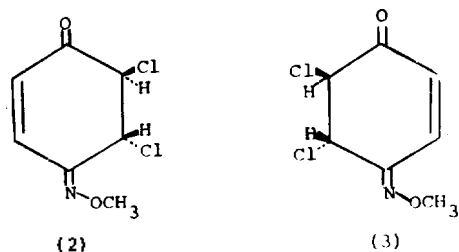
Energy   −135.9105 a.u   −135.9072 a.u

Conclusion

The chlorine addition and Diels–Alder cycloaddition of cyclopentadiene to 1, 4-benzoquinone-4-(O-methyloxime) occur to the quinone ring double bond which is oriented anti to the nitrogen lone pair giving rise to products of type (2) predominantly over the alternative configuration (3). This is seen to have resulted from an n-σ^* interaction between the nitrogen lone pair, n, and the app. vicinal bond, causing the π bond to be weakened and destabilization due to the less conjugation from reduced delocalization.

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