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### Triplet Carbonyl-Olefin Charge-Transfer Complexes. A CNDO Treatment

Sir:

Several reports have appeared recently in which the postulated exciplexes of  $n, \pi^*$  formaldehyde and ammonia have been examined theoretically.<sup>1</sup> However, in spite of the mounting evidence for the existence of  ${}^3n, \pi^*$  carbonyl-olefin exciplexes,<sup>2</sup> their existence has not been confirmed by any theoretical treatment.<sup>3</sup> Our interest in carbonyl-olefin photochemistry<sup>4</sup> has prompted us to apply the CNDO method to an investigation of excited-state complexes in these systems.

The exciplexes of  ${}^3n, \pi^*$  carbonyl compounds with olefins are thought to exhibit moderate charge-transfer (CT) character. Therefore the propensity of quinones to serve as electron acceptors might be expected to facilitate exciplex formation and to lead to high exciplex stabilization energies.<sup>5</sup> In the hopes that the existence of these more stable exciplexes might be more easily demonstrated than those arising from simple carbonyl compounds, we have examined the *p*-benzoquinone-ethylene ensemble by the CNDO method.

Calculations were performed for a large variety of geometries of the *p*-benzoquinone-ethylene system.<sup>6</sup> The procedure chosen was to use CNDO/2 to calculate ground-state (closed-shell singlet) energies as a function of geometry, and to calculate the singlet-triplet energy differences by CNDO/S, which is known to represent these quantities best.<sup>7</sup> Approaches along a vector connecting the carbonyl oxygen with the center of the ethylene double bond, both in the plane of the carbonyl  $\pi$  orbitals (geometries 1 and 3, Figure 1) and in the plane of the nonbonding orbitals (geometries 2 and 4, Figure 1), were examined systematically at distances of less than 2.00 Å. No matter what the direction of ethylene approach in the front oxygen hemisphere (angles 90-180°, Figure 1) the lowest singlet state was found to cross from the conventional ground state (little or no CT) to a CT state at separations of between 1.85 and 2.00 Å. In this crossing region the lowest triplet state drops below the singlet states (Figures 2 and 3a). In all four approach geometries, 1-4, a family of triplet minima as a function of the angle of approach,  $\alpha$ , could be assembled into a trough around the carbonyl oxygen. The minima of the cross sections of these troughs drop in energy, increase in depth below the singlet state, and move closer to the carbonyl oxygen as the approach angle  $\alpha$  goes from 90 to 180°. At 180°, approach geometries 1 and 2 converge to form a trough minimum which constitutes an *n* complex 5:  $D_{\min} = 1.86$  Å,  $\Delta E_{TS} = -19.7$  kcal/mol. In the same fashion approach geometries 3 and 4 converge to form another trough minimum which constitutes a  $\pi$  complex 6:  $D_{\min} = 1.90$  Å,  $\Delta E_{TS} = -17.3$  kcal/mol. Rotation about the carbonyl axis interconverts these two trough minima across an energy barrier of 7.7 kcal/mol.

It is encouraging to note that this type of complex is not

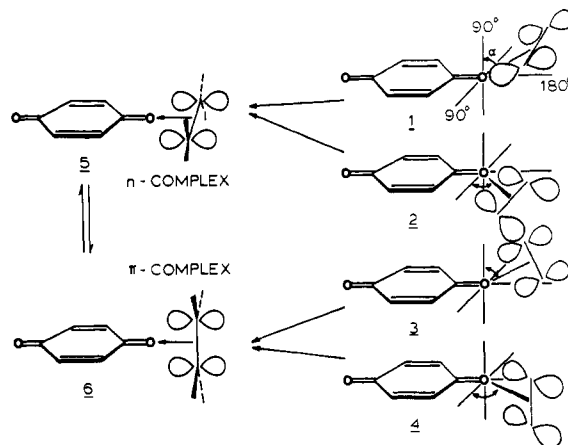


Figure 1. Carbonyl-olefin approach geometries, 1-4, and complex minimum geometries, 5 and 6.

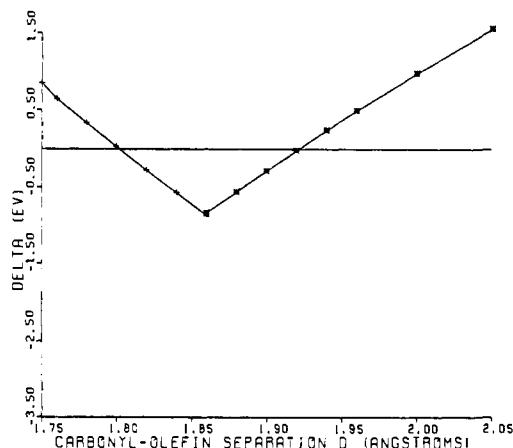


Figure 2. Energy differences,  $\Delta E_{TS}$ , between the lowest triplet,  ${}^3B_1$  ( $\dots 5b_1 12a_1$ ), and the lowest singlet state for approach geometry 5: to the right of the minimum  ${}^1A_1$  ( $\dots 12a_1 4b_1$ ) (conventional singlet), to the left of the minimum  ${}^1A_1$  ( $\dots 11a_1 5b_1$ ) (CT singlet).

Table I. CT Properties of Carbonyl-Olefin Complexes

	<i>p</i> -Benzoquinone-ethylene		Formaldehyde-ethylene	
	5	6	<i>n</i> complex	$\pi$ complex
Electrons transferred	0.4648	0.4707	0.4277	0.4647
Dipole moment, D	11.06	10.83	3.72	4.21

peculiar to *p*-benzoquinone, since the formaldehyde-ethylene<sup>6</sup> ensemble displays this same type of behavior in the 180° geometry: for the analogous *n* complex,  $D_{\min} = 1.92$  Å,  $\Delta E_{TS} = -2.0$  kcal/mol (Figure 3b); for the analogous  $\pi$  complex,  $D_{\min} = 1.94$  Å,  $\Delta E_{TS} = -0.2$  kcal/mol.

Both the *p*-benzoquinone and formaldehyde complexes are strongly CT in nature (see Table I) with the carbonyl component serving as the acceptor and the olefin as the donor. It should be noted that about the same amount of charge is transferred in all cases, but that the quinone complexes 5 and 6 have much higher dipole moments. The favorable delocalization of the transferred charge into the quinone  $\pi$  system accounts for these high moments and also probably accounts for the unusual stabilities of the triplet quinone complexes relative to the formaldehyde complexes where the transferred charge is of necessity localized on the carbonyl group. Since these complexes have little  $n, \pi^*$  character we tend to agree with Wagner, who has noted<sup>2c</sup> that photochemical species of this type should be classified as CT complexes rather than exciplexes.

The existence of CT complexes with these end-on geometries

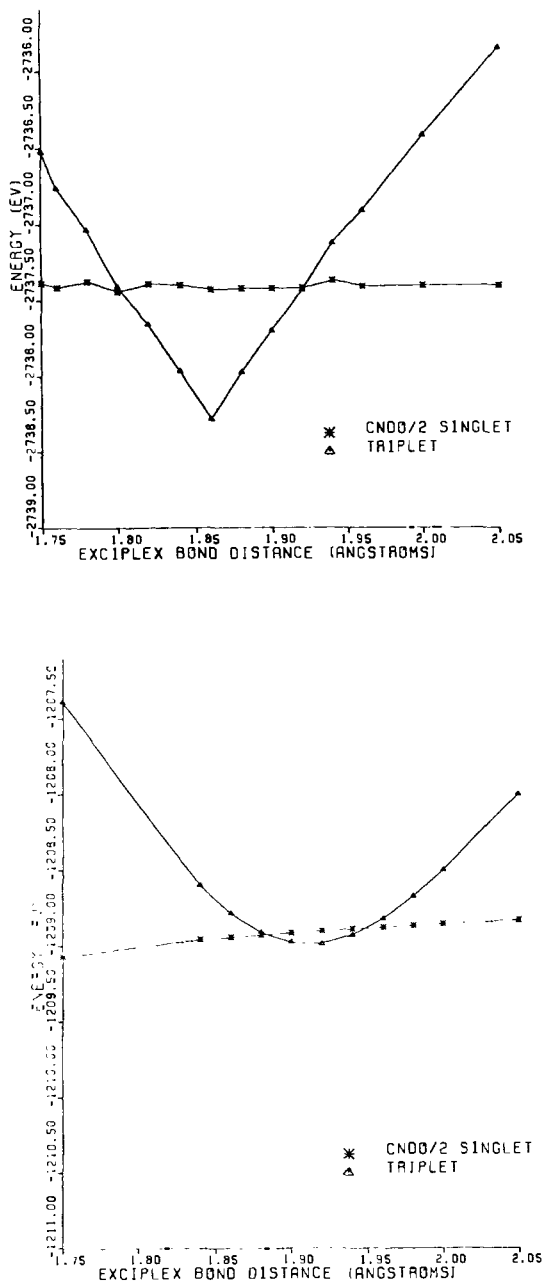
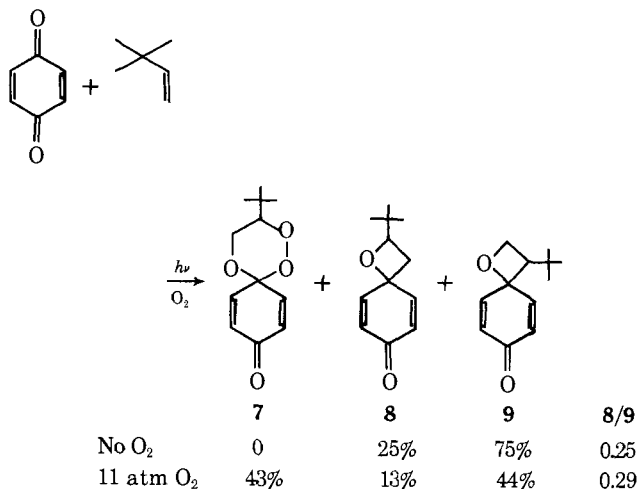


Figure 3. Energy profiles for the lowest singlet and lowest triplet states in a trough cross section for geometry 5: (a, top) *p*-benzoquinone-ethylene; (b, bottom) formaldehyde-ethylene.

formed from quinones, aldehydes, and presumably other types of carbonyl compounds has a number of intriguing photochemical implications. The singlet-triplet crossings associated with these complexes provide an explanation for the quenching of  $^3n, \pi^*$  ketones by olefins with high energy triplet states;<sup>2a,c,d,g</sup> the existence of two very similar end-on complexes related to 5 and 6 would account for Singer's observation of what he has termed  $n$  and  $\pi$  exciplexes.<sup>2g</sup> In our own work<sup>4,5</sup> the trapping of a *p*-benzoquinone CT complex by oxygen would account for the product distributions in Scheme I. Here the lack of variation of the oxetane isomer ratio (8/9) with oxygen pressure implies that the oxygen is not trapping the more stable preoxetane biradical, but instead is trapping a species that occurs before partitioning to the two preoxetane biradicals.

Finally it should be noted that carbonyl-olefin excited state complexes may exist at separations of greater than 2.00 Å.<sup>1</sup> While we are currently searching for these long range complexes, we feel that short range complexes such as the CT

Scheme I



complexes described here will have the greater influence upon excited-state chemistry.

### References and Notes

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### Immobilization of Synthetically Useful Enzymes by Condensation Polymerization

Sir:

We wish to describe a new procedure for the immobilization of enzymes in cross-linked organic polymer gels. This procedure rivals or surpasses in its operational simplicity and generality methods presently widely used (BrCN-agarose, glutaraldehyde, functionalized glass, preformed activated organic polymer gels),<sup>1</sup> and has proved especially valuable in immobilization of relatively delicate enzymes of interest for enzyme-catalyzed organic synthesis.<sup>2</sup>