

Photocycloaddition of coumarin and carbostyryl to olefins — An intermolecular orbital study

RITA CHADHA and N K RAY

Chemistry Department, University of Delhi, Delhi 110 007, India

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Abstract. The intermolecular orbital theory of Salem has been used to study the photocycloaddition reactions of coumarin and carbostyryl with 1-methoxy ethylene. Theoretical pathways have been drawn for the reactions and the magnitude of the π -electron stabilisation energy for the reactions has been calculated. All possible cycloaddition patterns have been examined and the relative importance of various interaction terms is discussed. Results of our calculations suggest that the bonds close in a concerted but asymmetric manner. The calculated regioselectivity correlates well with experimental data.

Keywords. Photocycloaddition ; reaction pathways ; molecular orbital study ; coumarins ; carbostyryls ; olefins.

1. Introduction

Recently, there has been a spurt of interest in cycloaddition reactions of conjugated systems (Song *et al* 1971 ; Hammond *et al* 1964 ; Hanifin and Cohen 1966 ; Evanega and Fabiny 1968 ; Julien and Foster 1973). Most of these studies were experimental in nature. Earlier theoretical studies were aimed at predicting qualitatively the regioselectivity, i.e. the preferred orientation of these reactions. However, to our knowledge, no attempt has yet been made to study the mechanistic aspects of photocycloaddition reactions of conjugated heterocyclic ketones like coumarin and carbostyryl.

In the present work, we have investigated the photochemical reactions of coumarin and carbostyryl with 1-methoxy ethylene. We have used the intermolecular theory of Salem (1968a) to predict the most favoured pathway and the preferred orientation of these reactions.

We have deliberately selected an unsymmetrical olefin, i.e., 1-methoxyethylene for our study to illustrate the regioselectivity of the cycloaddition reactions. A comparison of the reaction paths for coumarin and carbostyryl would illustrate the effect of substituting the oxygen atom in the heterocyclic ring of coumarin with a nitrogen atom. Moreover, the steric factors in the two systems are the same, while the electronic factors differ sufficiently for us to make a direct comparison.

2. Theoretical methods and models

The energies of interaction between the excited ketone and the ground state olefin have been estimated in terms of the perturbational treatment proposed by Salem (1968a). The π -electronic charges and energies of molecular orbitals, required for the calculation, have been computed by the Pariser-Parr-Pople (PPP) method (Pariser and Parr 1953; Pople 1953).

In Salem's approximation, the interaction energy between two conjugated molecules is described in terms of the π -electrons of the separate systems. An analytical expression for the interaction energy is obtained as a function of the overlaps between the $2p_z$ atomic overlaps of the two molecules.

This method makes use of three main assumptions. Firstly, the σ orbitals of both the molecules are not considered to take part in the reaction. The σ bonds act only as a hard core which does not permit too close an approach. Secondly, each atomic centre is thought to interact with only one centre of the other molecule. The overlap integrals are assumed to be small compared to unity (i.e., ≤ 0.2).

Figure 1 illustrates the energy level diagram for the excited ketones ($\psi_6 \rightarrow \psi_7$ configuration) and 1-methoxy ethylene. It is obvious that the highest occupied MOs (HOMOs) of coumarin and carbostyryl are nearly degenerate with the

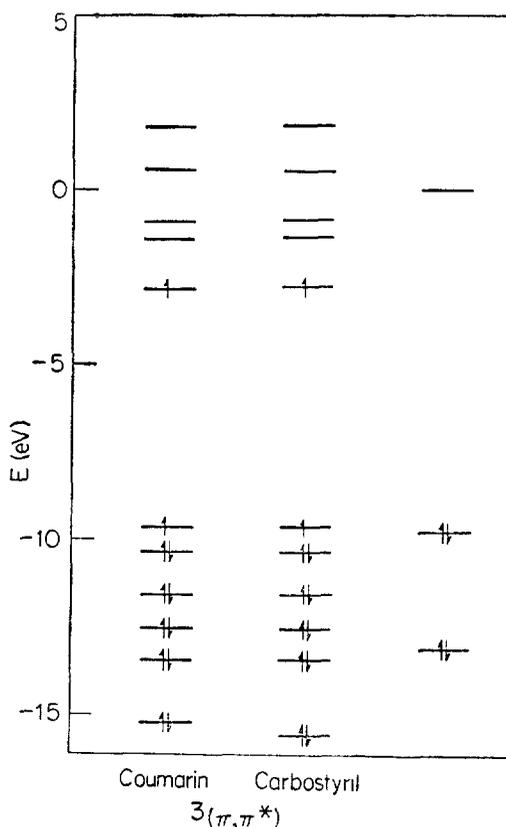


Figure 1. The PPP energy level diagram for excited coumarin and carbostyryl ($\psi_6 \rightarrow \psi_7$ configuration) and 1-methoxy ethylene.

HOMO of 1-methoxy ethylene. The HOMOs of the interacting molecules are therefore close enough for there to be first order perturbational interaction between these orbitals.

3. Results and discussion

The photoreactive excited state of coumarins is of the $^3(\pi, \pi^*)$ type, as evidenced by the spectroscopic results of Song *et al* (1971). However, according to them, the reactivity of the singlet $^1(\pi, \pi^*)$ state cannot be ruled out. It must be emphasised here that, while elucidating the mechanism of a photochemical reaction i.e. whether a reaction is concerted or not, we are talking only of reactions in excited singlet states, since reactions in triplet states generally occur *via* a two-step mechanism because of spin requirements.

Interactions through four-centre unions have been calculated. Both possible orientations of addition have been studied.

The different orientations of addition for coumarin and carbostyryl are shown in figure 2 (*a* and *b* for coumarin and *c* and *d* for carbostyryl). For mode *a* of cycloaddition of coumarin to 1-methoxy ethylene, the energy of thermal interaction, as a function of overlaps, is

$$E_{int} = 7.719 S_{31'}^2 + 7.241 S_{42'}^2 + 17.259 S_{31'} S_{42'} \quad (1)$$

and the equation of the reaction surface is

$$S_{31'}/S_{42'} = \frac{15.439S_{31'} + 17.259S_{42'}}{17.259S_{31'} + 14.482S_{42'}} \quad (2)$$

From equation (1) it is obvious that the interaction energy is positive whatever the magnitude of the two overlaps. Hence the thermal reaction is not favoured and the overall activation energy is 1.289 eV. The plot of the reaction surface is shown in figure 3 and the reaction is seen to be concerted, almost symmetric

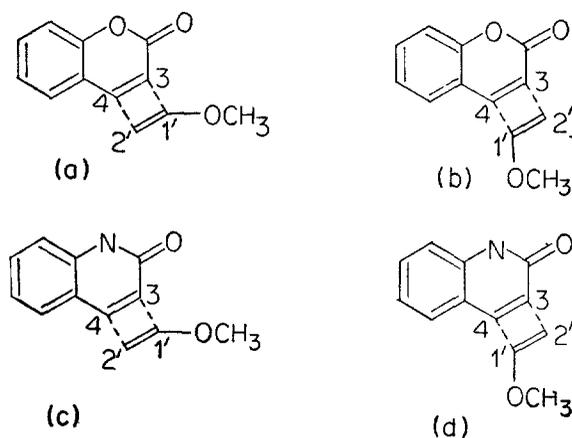


Figure 2. The different modes of cycloaddition of coumarin and carbostyryl to 1-methoxy ethylene.

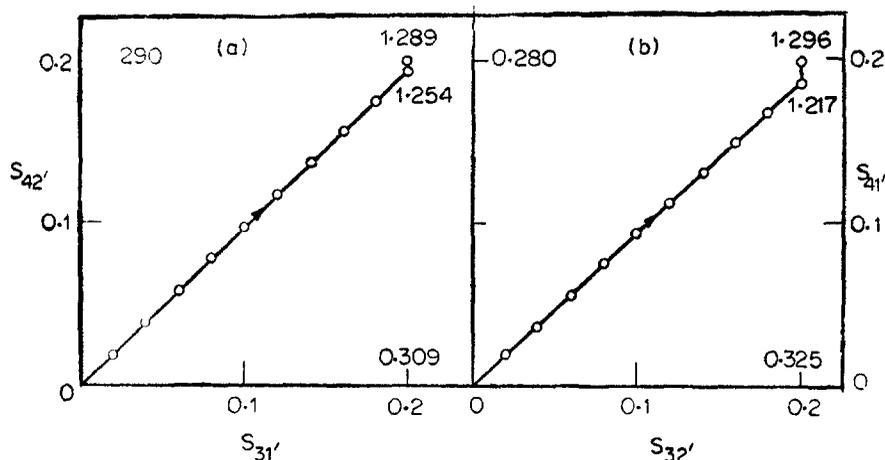


Figure 3. Reaction paths for thermal cycloaddition of coumarin to 1-methoxy ethylene. Paths require activation energy.

(for $S_{31'} = 0.2$, $S_{42'} = 0.195$ and $E_{int} = 1.254$ eV) and requiring activation energy along its whole path.

For the second orientation (*b* in figure 2), the thermal interaction energy equation is

$$E_{int} = 8.135S_{32'}^2 + 6.997S_{41'}^2 + 17.259S_{32'}S_{41'}, \quad (3)$$

and
$$S_{32'}/S_{41'} = (16.270S_{32'} + 17.259S_{41'}) / (17.259S_{32'} + 13.994S_{41'}). \quad (4)$$

The reaction path, shown in figure 3(b), is similar to that for mode *a*, except that it has greater asymmetry. When the 32' bond has been established, ($S_{32'} = 0.2$), the value of the 41' bond overlap, $S_{41'}$, is only equal to 0.187, and the activation energy required to obtain this asymmetric configuration is 1.217 eV. The 41' bond then closes, the activation energy required for this being 0.079 eV. The activation energy required for the complete reaction is 1.296 eV.

For carbostyryl, the thermal interaction energy equations for interaction *c* and *d*, respectively, are given in (5) and (6)

$$E_{int} = 7.720S_{31'}^2 + 7.279S_{42'}^2 + 17.240S_{31'}S_{42'}, \quad (5)$$

$$E_{int} = 8.139S_{32'}^2 + 7.025S_{41'}^2 + 17.240S_{32'}S_{41'}. \quad (6)$$

The activation energy for interaction *c* is 1.290 eV. The reaction path *d* has greater asymmetry and the activation energy required to obtain the asymmetric configuration is 1.219 eV (see figure 3).

From the results given above, it appears that thermal cycloaddition is not favoured in any of the four cases studied here. However, the activation energies along the reaction path are lower for *b* and *d* as compared with those for *a* and *c* respectively.

For the photochemical reaction corresponding to mode *a* of interaction of coumarin with 1-methoxy ethylene, the interaction energy is given by,

$$E_{int}^* = 5.352S_{32'}^2 - 2.206S_{31'} + 7.356S_{42'}^2 - 1.929S_{42'} + 6.316S_{31'}S_{42'} \quad (7)$$

and the reaction path equation is

$$S_{31}'/S_{42}' = \frac{10.704S_{31}' + 6.316S_{42}' - 2.206}{6.316S_{31}' + 14.712S_{42}' - 1.929} \quad (8)$$

The plot of the reaction path is shown in figure 4. Initially, when

$S_{31}' \simeq S_{42}' \simeq 0.0$, the slope is

$$\frac{S_{42}'}{S_{31}'} = \frac{1.929}{2.206} = 0.874.$$

Therefore, the reaction starts off almost symmetrically. As the molecules get closer, the second order effects begin to operate. The second order repulsion is greater along the S_{42}' reaction coordinate, although the first order attraction is weaker along this coordinate. In equation (7), all the second order terms, including the cross-term, are large and repulsive. Because of the asymmetry in the terms for

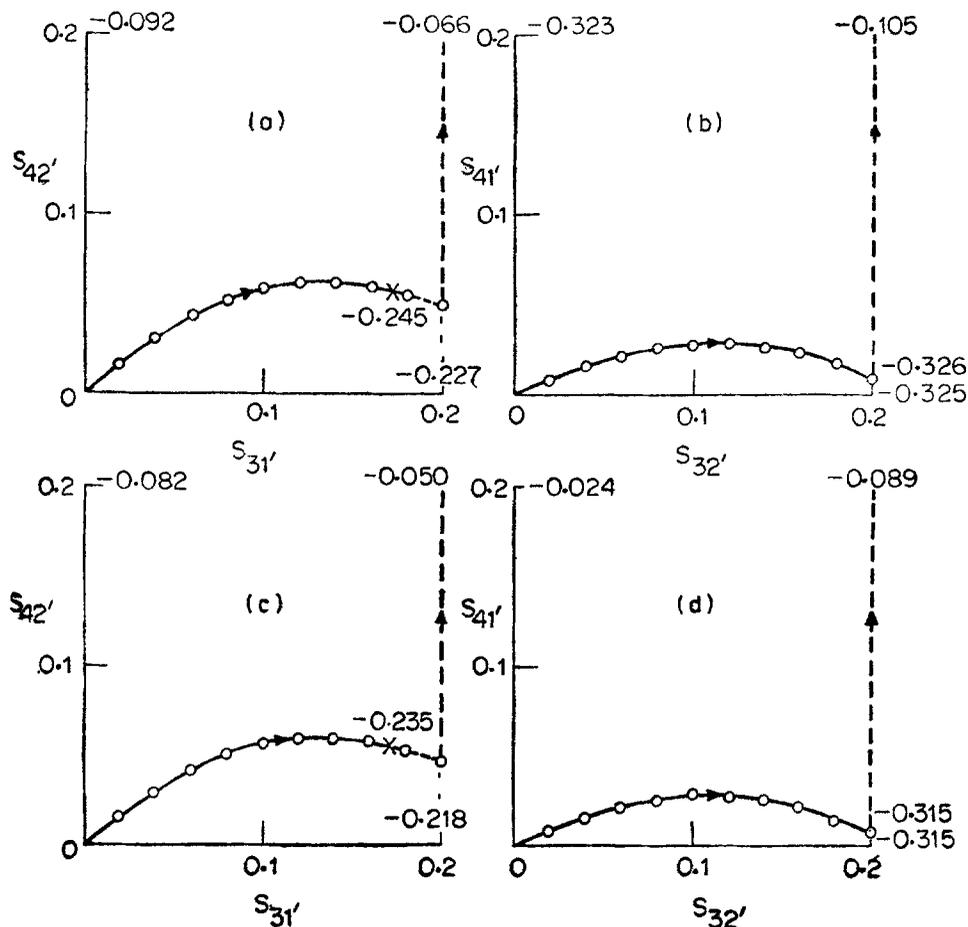


Figure 4. Pathways for photochemical cycloaddition of coumarin and carbostyryl to 1-methoxy ethylene.

the two reaction coordinates, the reaction path is asymmetric, the 31' bond closing faster than the 42' bond. Both the linear terms are negative and hence reinforce each other. As $S_{31'}$ increases, the value of $S_{42'}$ at first increases, until it reaches a value of 0.062 for $S_{31'} = 0.133$ and then falls off to 0.049 for $S_{31'} = 0.2$ ($E_{\text{int}}^* = -0.242$ eV for $S_{31'} = 0.2$ and $S_{42'} = 0.049$). Hence the π -electron stabilisation energy is maximum if the cycloaddition starts off by an almost pure 31' bond closure. The most stable intermediate along the reaction path corresponds to $S_{31'} = 0.172$, $S_{42'} = 0.057$ and $E_{\text{int}}^* = -0.245$ eV. After this asymmetric configuration is reached, there is some activation energy (0.179 eV) required to acquire the totally symmetric configuration in which both bonds have been formed. The overall stabilisation energy is -0.066 eV.

For the other possible orientation of cycloaddition of coumarin to 1-methoxy ethylene (mode *b*, see figure 2), the energy of interaction is given by

$$E_{\text{int}}^* = 7.181S_{32'}^2 - 3.061S_{32'} + 6.143S_{41'}^2 - 1.390S_{41'} + 6.316S_{32'}S_{41'}, \quad (9)$$

and the reaction path equation is

$$S_{32'}/S_{41'} = \frac{14.362S_{32'} + 6.316S_{41'} - 3.061}{6.316S_{32'} + 12.286S_{41'} - 1.390}. \quad (10)$$

Initially, $S_{41'}/S_{32'} = 0.454$. This ratio is much smaller than that for reaction *a*. Therefore, in this reaction $S_{41'}$ remains quite small and quickly reaches a maximum value of 0.029 for $S_{31'} = 0.115$, and then falls off to 0.01 for $S_{32'} = 0.2$. This is the most stable configuration along the reaction path, and the π -stabilisation energy for this configuration is -0.326 eV. The activation energy required for the reaction to proceed to completion is 0.221 eV and hence the overall stabilisation energy is -0.105 eV.

From the above results it appears that both reactions are favoured more along one reaction axis and are both concerted and asymmetric. The term 'concerted' is actually a misnomer when applied to these reactions, since some π -activation energy is required between the intermediate asymmetric configuration and the totally symmetric one. If the reactions were to occur by a two-step mechanism, more π -activation energy would have been required for the second step. Another fact that emerges from our discussion is the fact that mode *b* is favoured over mode *a*. This is in agreement with the experimental data of Hanifin and Cohen (1966).

The reaction paths for orientations *c* and *d* of photocycloaddition of carbostyryl to 1-methoxy ethylene are similar to those for orientations *a* and *b* for coumarin, respectively. The expression for the energy of interaction as a function of overlaps, for mode *c*, is

$$E_{\text{int}}^* = 5.396S_{31'}^2 - 2.171S_{31'} + 7.348S_{42'}^2 - 1.878S_{42'} + 6.255S_{31'}S_{42'}, \quad (11)$$

and the equation for the reaction path is

$$S_{31'}/S_{42'} = \frac{10.792S_{31'} + 6.255S_{42'} - 2.171}{6.255S_{31'} + 14.696S_{42'} - 1.878}. \quad (12)$$

Initially, the ratio $S_{42'}/S_{31'} = 1.878/2.171 = 0.865$, and $S_{42'}$ increases with $S_{31'}$ until it reaches a value of 0.060 for $S_{31'} = 0.131$. Further increase in the 31' overlap results in a slight decrease in the 42' overlap until it becomes equal to 0.056 for $S_{31'} = 0.169$. This asymmetric configuration is the most stable one along the reaction path ($E_{\text{int}}^* = -0.235$ eV). Further increase in the 31' overlap requires activation energy until a configuration in which $S_{31'} = 0.2$ and $S_{42'} = 0.047$ is reached. In other words, the 31' bond closes first. The activation energy required to complete the reaction after the most stable configuration is reached is 0.185 eV and the net stabilisation energy is -0.050 eV.

The equations for d are quite similar to those for mode b of coumarin. The relevant expressions are

$$E_{\text{int}}^* = 7.194S_{32'}^2 - 3.012S_{32'} + 6.153S_{41'}^2 - 1.350S_{41'} + 6.255S_{32'}S_{41'} \quad (13)$$

$$\text{and } S_{32'}/S_{41'} = \frac{14.388S_{32'} + 6.255S_{41'} - 3.012}{6.255S_{32'} + 12.306S_{41'} - 1.350} \quad (14)$$

The reaction path shown in figure 4 is similar to that for b . When $S_{32'} = 0.2$, $S_{41'}$ has a value of only 0.008 and the interaction energy corresponding to this configuration is -0.315 eV. The 41' bond then closes with an activation energy of 0.226 eV and the effective stabilisation energy is -0.089 eV.

Again it can be seen that, for carbostyryl, the interaction corresponding to mode d (see figure 2) is more facile than that corresponding to c since the π -stabilisation energy along the reaction path is more negative for this configuration. The total π -stabilisation energy is also greater for this reaction. Hence mode d is the preferred mode of ring closure for the photocycloaddition of 1-methoxy ethylene to carbostyryl and this prediction is in agreement with experiment (Evanega and Fabiny 1968).

$\Delta E_{\text{int}}(j \rightarrow k)$, the change in the interaction energy due to excitation, can be written as a sum of individual contributions

$$\Delta E_{\text{int}}(j \rightarrow k) = \Delta E_{H'}(1) + \Delta E_{\text{size}} + \Delta E_{H'}(2) + \Delta E_{k'}(2) \quad (15)$$

where $\Delta E_{H'}(1)$ represents the first order interaction energy between the HOMOs of the two molecules; ΔE_{size} is the size effect resulting from the excitation of an electron from the HOMO to the LUMO of the ring compound; $\Delta E_{H'}(2)$ and $\Delta E_{k'}(2)$ are the second order interaction terms resulting from the interaction of the orbitals of 1-methoxy ethylene with the HOMO and LUMO, respectively, of coumarin/carbostyryl.

In table 1 we show the relative contributions of these four terms to $\Delta E_{\text{int}}(j \rightarrow k)$. A glance at this table reveals the following facts. Firstly, there is predominance of attractive forces and hence the overall interaction energy is negative. The largest contribution comes from the first order term, $\Delta E_{H'}(1)$. The second largest attraction term is $\Delta E_{k'}(2)$. $\Delta E_{H'}(2)$ also makes a small, negative contribution. The only positive term is ΔE_{size} , but this is quite small.

Table 1. The contribution of various terms to $\Delta E_{\text{int}} (j \rightarrow k)$

System	Mode ^a of Interaction	$\Delta E_{jj'} (1)$	$\Delta E_{\text{int}e}$	$\Delta E_{jj'} (2)$	$\Delta E_{\text{int}e'} (2)$	Total $\Delta E_{\text{int}} (j \rightarrow k)$
Coumarin	<i>a</i> ^b	-0.827	0.027	-0.104	-0.451	-1.355
	<i>b</i> ^c	-0.890	0.027	-0.081	-0.456	-1.400
Carbostyryl	<i>c</i> ^b	-0.810	0.033	-0.099	-0.463	-1.339
	<i>d</i> ^c	-0.873	0.033	-0.076	-0.469	-1.385

^a See figure 2

^b Calculated for $S_{31'} = S_{41'} = 0.2$

^c Calculated for $S_{32'} = S_{42'} = 0.2$

4. Conclusions

The theoretical pathways for the photocycloaddition of coumarin and carbostyryl to ethylene are consistent with experimental data. Experimentally it has been found that coumarin undergoes sensitised photocycloaddition to olefins (Hanifin and Cohen 1966) to yield the cyclobutene adduct. It is significant that no oxetane is formed by the addition of the olefin to the carbonyl bond of coumarin. In fact, our calculations indicate that photoaddition to the carbonyl bonds of coumarin and carbostyryl requires considerable activation energy (0.6 to 0.8 eV).

The photoreactivity of carbostyryl is similar to that of coumarin. With a 6.4 : 1 molar ratio of 1-methoxy ethylene to carbostyryl, the adduct was obtained in 65% yield, while the dimer was obtained in 35% yield (Evanega and Fabiny 1968). Our calculations indicate that photodimerisation is not preferred because of the comparatively low π stabilisation energies (~ -0.34 eV).

It is noteworthy that, although *cis* ring fusion prevails, only one adduct is formed (i.e. *b* for coumarin and *d* for carbostyryl). Corey *et al* (1964) and Evanega and Fabiny (1968) have rationalised this observation in terms of the electron density distribution in the excited species. They have based their discussion on the electron density distribution in the (n, π^*) excited state. It has, however, been shown (Song *et al* 1971) that the photoreactive excited state of coumarin and presumably of carbostyryl, too, is the (π, π^*) state. The calculated PPP electron density distributions (Ray and Ahuja 1973; Sairam and Ray 1979) for the $^1(\pi, \pi^*)$ and $^3(\pi, \pi^*)$ states of coumarin and carbostyryl correlate well with the observed regioselectivity. Hence both charge and overlap effects favour the formation of *b* and *d* over *a* and *c*, respectively.

In conclusion, we would like to add that in the photocycloaddition reactions of coumarin/carbostyryl with 1-methoxy ethylene, the dominant attraction terms [i.e. $\Delta E_{jj'} (1)$ and $\Delta E_{\text{int}e'} (2)$] essentially determine the course of reaction and the favoured products are *b* and *d*, instead of *a* and *c* (see figure 2). These

results indicate that even the very simple intermolecular orbital theory of Salem (1968a) is quite adequate for predicting the course of cycloaddition reactions, both thermal and photochemical, for coumarin and its aza analog, i.e. carbostyryl.

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