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Nucleophilic attack on ketene, 6-methylene-2,4-cyclohexadienylideneketene, 6-oxo-2,4-cyclohexadienylideneketene and 4-oxo-2,5-cyclohexadienylideneketene: an *ab initio* study

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epoc ABSTRACT: Nucleophilic attack of cyanide anion at the carbonyl carbon was studied computationally at the MP2/6–311+G** level for ketene and at the MP2/6–31+G* and MP2/6–31+G*//HF/6–31+G* levels for all four title compounds. Heats of addition were computed for formation of in-plane adducts and perpendicular adducts where the terms 'in-plane' and 'perpendicular' indicate the direction of nucleophilic attack relative to the ketene plane. Heats of activation were also computed for the two modes of attack. For ketene (**1**) the in-plane adduct is favored by 37.6 kcal mol^{-1} and the in-plane transition state by 18.8 kcal mol^{-1}. For the 6-methylene compound (**2**) the in-plane adduct is favored by 20.1 kcal mol^{-1} and the in-plane transition state by 7.3 kcal mol^{-1}. For the 6-oxo compound (**3**) the in-plane adduct is more stable by 11.2 kcal mol^{-1} whereas the in-plane transition state is preferred by 8.8 kcal mol^{-1}. For the 4-oxo compound (**4**) the in-plane adduct is favored by 19.3 kcal mol^{-1} but its transition state by only 2.8 kcal mol^{-1}. The in-plane adduct for ketene is the enolate of acetyl cyanide while the perpendicular adduct is a pyramidalized carbanion attached to a cyanocarbonyl group. Calculated NPA charges support this conclusion. The perpendicular adduct is actually the transition state for rotation about the C—C bond of the ketene moiety in the in-plane adduct, and the 37.6 kcal mol^{-1} enthalpy difference is closely matched by the calculated activation enthalpy for rotation about the C—C bond of acetaldehyde enolate: $\Delta H^{\ddagger} = 33.6$ kcal mol^{-1}. The smaller differences found for in-plane vs perpendicular adduct formation for the 6-methylene, 6-oxo and 4-oxo compounds are correlated with decreases in bond length alternation within the six-membered rings which occur upon addition of the nucleophile. Less alternation may be associated with an approach to aromaticity, hence an increase in stability. Both modes of attack lead to reduced bond length alternation, but the amount of alternation is lowered more for the perpendicular adducts than for the in-plane adducts. Changes in the C—O bond lengths are also diagnostic. For all four ketenes the ketenyl C═O length in the in-plane adducts is greater than in the perpendicular adducts reflecting more single bond (enolate) character in the former and more double bond (carbonyl) character in the latter. On the other hand the lengths of the 6-oxo and 4-oxo C—O bonds in their in-plane adducts are smaller than in the perpendicular adducts, consistent with increased conjugation with the oxo substituent in the latter. The greater NPA charge on the 6-oxo and 4-oxo oxygens of the perpendicular adducts supports this conclusion. Calculated enthalpies of activation are in the order ketene > 6-methyleneketene > 6-oxoketene, in qualitative agreement with experimentally determined rates of hydration. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: ketene; conjugated ketenes; nucleophilic addition; *ab initio* calculations

INTRODUCTION

Nucleophilic addition is one of the most characteristic reactions of ketenes. Oxygen, nitrogen, sulfur, and carbon nucleophiles have all been found to add readily:

$$R_1R_2C_\beta{=}C_\alpha{=}O + Nu{-}H \rightarrow R_1R_2CH{-}C(Nu){=}O \quad (1)$$

In fact the generation of short-lived ketenes has often been implicated by detection of products derived from nucleophilic trapping. Experimental evidence relating to the mechanisms of these additions has been reviewed in detail by Seikaly and Tidwell.[1,2] Among other features, the attack of the nucleophile on the α-carbon occurs in the plane of the ketene skeleton,[3] a result supported by molecular orbital calculations which reveal a large coefficient of the LUMO at C_α in the ketene plane.[4] Although this result is generally accepted for typical ketenes, it has been suggested that for the cyclic, conjugated ketene 4-oxo-2,5-cyclohexadienylidineketene (4-OCDK) (**4**),[5] and

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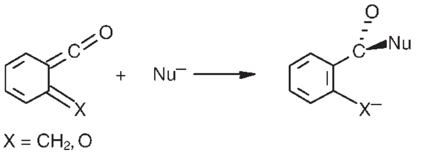
by analogy, 6-methylene-2,4-cyclohexadienylidineketene (6-MCDK) (**2**) and 6-oxo-2,4-cyclohexadienylidineketene (6-OCDK) (**3**), that attack perpendicular to the ketene plane is preferred. Both **2**[6] and **3**[7] react with water much faster than do either ketene[8] or a saturated cyclic analog, pentamethyleneketene,[9] and it might be inferred that perpendicular attack could aromatize the ring thereby imparting extra stability to the transition state:



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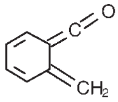
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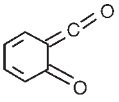
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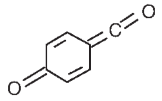
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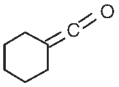
pentamethyeneketene

In this paper, we report an *ab initio* computational study of the addition of nucleophilic cyanide anion to ketene itself and to ketenes **2**, **3** and **4**. Adducts and transition states are calculated both for in-plane and perpendicular nucleophilic attack on all four ketenes. Previous computational work on the addition of nucleophiles to ketenes, including oxoketenes, has been reported and discussed by Tidwell and co-workers.[2, 7]

METHODS

For the reactions of ketene with cyanide, calculations were carried out at the MP2/6–311+G** level and also at the lower MP2/6–31+G* and MP2/6–31+G*//HF/6–31+G* levels using the Gaussian 94[10] and Gaussian 98[11] quantum mechanical packages. This was done in order to assess the performance at the lower levels relative to the higher level. As can be seen from Table 1, the reaction and activation enthalpies obtained by all three methods are in good qualitative agreement. It was important to establish acceptable performance at the lower levels because they were used for the larger systems associated with compounds **2**, **3** and **4**. Zero-point vibrational energies (ZPVEs) were calculated at the HF/6–311+G** or HF/6–31+G* levels and scaled according to the recommendations of Scott and Radom.[12] Previous work has shown that the use of ZPVEs calculated at the HF/6–311+G** level and applied to MP2/6–311+G** electronic energies leads to negligible errors, compared with the use of MP2/6–311+G** ZPVEs, in computed ΔH_{RXN} values.[13]

For three transition state structures in the 6-methylene and 6-oxo series, convergence at the MP2/6–31+G* level was not obtained. At the MP2 level the nucleophile drifted away from the ketene, indicative of barrier-free addition at this level. Therefore, we report single-point MP2/6–31+G*//HF/6–31+G* energies (i.e. MP2 energies calculated for the optimized HF geometries) as well as the fully optimized MP2 energies for the compounds which *did* converge at that level. As can be seen from Table 2, the effects on ΔH values are inconsequential. We note here that almost all the calculated transition states for reactions of **2**, **3** and **4** are early in the sense that the nucleophile-electrophile distances are long (see Table 4). Moreover, the transition state energies are well below those of the reactants, and are in the range expected for anion–molecule complexes (Table 2). It seems likely that those transition states successfully calculated at MP2/6–31+G* represent small bumps separating ion–molecule complexes from the addition products, and that in those cases in which convergence was not achieved at that level

Table 1. Enthalpies of reaction and activation and isomerization for addition of cyanide to ketene (**1**) (kcal mol^{-1})[a]

Process	MP2/6–311+G**	MP2/6–31+G*//HF/6–31+G*	MP2/6–31+G*
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ad-ip) (in-plane cyano adduct)	−26.8	−28.0	−28.3
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ad-s-perp) (*syn* perpendicular cyano adduct)	10.8	12.5	11.7
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ts-ip)[b] (in-plane cyano ts)	−5.3	−6.9	−5.3
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ts-s-perp)[c] (*syn* perpendicular ts)	13.5	15.3	14.5
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ad-nc-ip) (in-plane isocyano adduct)	−8.6	NA	NA
$\mathbf{1} + \mathrm{CN}^- \rightarrow \mathbf{1}$(ts-nc-ip) (in-plane isocyano ts)	−4.4	NA	NA
$\mathbf{1}$(ad-s-perp) $\rightarrow \mathbf{1}$(ad-a-perp)[c]	1.6	1.0	1.0
$\mathbf{1}$(ts-ip) $\rightarrow \mathbf{1}$(ts-s-perp)[c]	18.8	22.2	19.8

[a] ΔE values were corrected for ZPVE differences. ZPVEs were calculated at the HF/6–31+G* level and scaled by 0.9153 for the 6–31+G* basis set, and at HF/6–311+G** and scaled by 0.9135 for the 6–311+G** basis set, as recommended by Scott and Radom,[12] but no further (thermal) corrections were applied.
[b] Enthalpies of activation.
[c] Enthalpies of isomerization.

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Table 2. Enthalpies of reaction, activation and isomerization for addition of cyanide to 6-methylene-2,4-cyclohexadienylidineketene (**2**), 6-oxo-2,4-cyclohexadienylideneketene (**3**) and 4-oxo-2,5-cyclohexadienylidineketene (**4**) (kcal mol^{-1})[a]

Compound	Process	MP2/6–31+G* //HF/6–31+G*	MP2/6–31+G*
2	**2** + CN^{-} $\rightarrow$ **2**(ad-a-ip) (in-plane adduct, *anti*)	−51.0	−52.5
	2+CN^{-} $\rightarrow$ **2**(ad-perp) (perpendicular adduct)	−30.9	−31.5
	2 + CN^{-} $\rightarrow$ **2**(ts-a-ip)[b] (in-plane ts)	−15.4	NA
	2 + CN^{-} $\rightarrow$ **2**(ts-perp)[b] (perpendicular ts)	−8.1	−7.4
	2(ad-a-ip) $\rightarrow$ **2**(ad-perp)[c]	20.1	21.0
	2(ts-a-ip) $\rightarrow$ **2**(ts-perp)[c]	7.3	NA
3	**3** + CN^{-} $\rightarrow$ **3**(ad-s-ip) (*syn* in-plane adduct)	−55.8	−56.1
	3 + CN^{-} $\rightarrow$ **3**(ad-s-ip)- (*anti* in-plane adduct)	52.5	−52.9
	3 + CN^{-} $\rightarrow$ **3**(ad-perp) (perpendicular adduct)	−44.6	−45.5
	3 + CN^{-} $\rightarrow$ **3**(ts-a-ip)[b] (in-plane ts)	−22.2	NA
	3 + CN^{-} $\rightarrow$ **3**(ts-perp)[b] (perpendicular ts)	−13.4	NA
	3(ad-s-ip) $\rightarrow$ **3**(ad-perp)[c]	11.2	10.6
	3(ad-s-ip) $\rightarrow$ **3**(ad-a-ip)[c]	3.3	3.2
	3(ts-a-ip) $\rightarrow$ **3**(ts-perp)[c]	8.8	NA
4	**4** + CN^{-} $\rightarrow$ **4**(ad-ip) (in-plane adduct)	−66.0	−66.1
	4 + CN^{-} $\rightarrow$ **4**(ad-perp) (perpendicular adduct)	−47.0	−46.8
	4 + CN^{-} $\rightarrow$ **4**(ad-oxo) (oxo adduct)	0.2	0.6
	4 + CN^{-} $\rightarrow$ **4**(ts-ip) (in-plane ts)	−18.8	−19.5
	4 + CN^{-} $\rightarrow$ **4**(ts-perp) (perpendicular ts)	−18.8	−16.7
	4(ad-ip) $\rightarrow$ **4**(ad-perp)[c]	19.0	19.3
	4(ad-ip) $\rightarrow$ **4**(ad-oxo)[c]	66.2	66.7
	4(ts-ip) $\rightarrow$ **4**(ts-perp)[c]	0.0	2.8

[a] ΔE values were corrected for ZPVE differences. ZPVEs were calculated at the HF/6–31+G* level and scaled by 0.9153 as recommended by Scott and Radom,[12] but no further (thermal) corrections were applied.

[b] Enthalpies of activation.

[c] Enthalpies of isomerization.

the reaction has a very small or non-existent barrier. Attempts to calculate the ion–molecule complexes were not successful, but led to addition.

In-plane adducts in the 6-methylene, 6-oxo and 4-oxo series were constructed in two ways. In the first way, the rings were built as *exo*-methylene or *exo*-oxo cyclohexadiene moieties. In the second way, a benzene core was used. The two ways produced identical results.

Adducts formed by attack perpendicular to the plane defined by the ketene moiety were also investigated in two ways. In one way a constraint was applied so that rotation to the in-plane structure would not occur. For ketene itself this was done by requiring the H—C—C—CN (or H—C—C—NC) dihedrals to be equal, thus ensuring C_s symmetry. For the reactions in the 6-methylene, 6-oxo and 4-oxo systems, one of the dihedral angles defined by the cyano carbon, the ketenyl α-carbon, and two adjacent ring carbons was fixed at 90°. In the second way, the perpendicular adducts of ketenes **2**, **3** and **4** were calculated as the transition states for rotation about the C_β—C_α bond of the more stable, in-plane adducts. The resulting structures have dihedral angles within 10 degrees of perpendicularity. Calculated energies using the two methods were in good agreement, and each structure has a single imaginary frequency corresponding to rotation toward the in-plane adduct. Energies obtained using the second method are preferred as they reflect no artificial constraints.

The 'transition states' for addition in the perpendicular manner were calculated by enforcing the 90° dihedral angle of approach. The resulting structures are not true transition states, but second-order saddle points each with two imaginary frequencies, one corresponding to the reaction coordinate for addition and the other to rotation about the C_β—C_α bond. Nevertheless, these structures are taken as useful approximate models for the perpendicular transition states. The energetic differences between in-plane and perpendicular attack are usually so large that small errors caused by the use of these models are not significant.

Natural population analysis (NPA) charges were computed for structures optimized at the MP2/6–311+G** level for the ketene series, and at MP2/6–31+G* level for ketenes **2**, **3** and **4**.

RESULTS AND DISCUSSION

Ketene

Several nucleophiles were examined to determine the exo- or endothermicity of their addition reactions to ketene. There is a delicate balance between the nucleophilicity and the leaving group ability (nucleofugality) of the nucleophile. Among the halides, fluoride forms the in-plane adduct highly exothermically. The adducts of chloride and bromide, on the other hand, are not stable, but dissociate to anion–molecule complexes. Bicarbonate forms a stable in-plane adduct with ketene, but the O—C bond length is unusually long at 1.66 Å (MP2/6–31+G* geometry). Cyanide, attacking either as a carbon-centered nucleophile (cyanide) or as a nitrogen-centered nucleophile (isocyanide), forms stable in-plane adducts with normal nucleophile-carbon lengths: 1.50 Å in the cyanide adduct and 1.52 Å in the isocyanide adduct (MP2/6–311+G** geometries); see Table 3. However, in the perpendicular adducts these lengths have increased. For the perpendicular cyanide adduct a modest lengthening to 1.54 Å can be attributed to negative hyperconjugation. In the perpendicular isocyanide adduct (HF/6–311+G** geometry) an additional increase to 1.57 Å has occurred. For the perpendicular isocyanide transition state the distance is longer still. In fact at MP2/6–311+G** both the perpendicular isocyanide adduct *and*

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Table 3. Selected geometric features of ketene, its cyanide and hydride adducts and the transition states for addition of cyanide[a]

Compound	*d*(C—O) (Å)	*d*(CH_2—C) (Å)	*d*(C—X) (Å)[b]	Φ (H—C—H), (°)	Φ (O—C—C), (°)	Change at ts[c] (%)
1 ketene	1.168	1.322	NA	121.8	180.0	NA
1(ad-ip) (in-plane cyano adduct)	1.267	1.387	1.502	119.9	131.5	NA
1(ad-s-perp) (perp, *syn* cyano adduct)	1.227	1.463	1.542	104.5	130.1	NA
1(ts-ip) (in-plane cyano ts)	1.173	1.334	2.642	123.9	164.8	5.0
1(ts-s-perp) (perp, *syn* cyano ts)	1.191	1.415	1.902	107.8	140.6	39
1(ad-nc-ip) (in-plane isocyano adduct)	1.243	1.378	1.516	120.4	134.8	NA
1(ad-s-perp) (perp, *syn* isocyano adduct)[d]	1.172	1.460	1.570	105.1	134.3	NA
1(ts-nc-ip) (in-plane isocyano ts)	1.183	1.347	2.109	122.7	154.1	20
1(ts-s-perp) (perp, *syn* isocyano ts)[d]	1.165	1.450	1.636	105.9	136.6	81[d]
5 acetaldehyde enolate	1.271	1.390	1.125	119.2	130.1	NA
6 acetaldehyde enolate, perpendicular	1.232	1.480	1.139	104.0	128.0	NA
7 allyl anion	1.399[e]	1.399[e]	1.099	117.7	131.6[f]	NA
8 allyl anion, perp	1.353[e]	1.491[e]	1.114	106.7	125.0[f]	NA

[a] Geometries were optimized at MP2/6–311+G** except where indicated.

[b] X stands for the nucleophilic atom in adduct formation: carbon for addition of cyanide, nitrogen for the isocyanide adduct, hydrogen for the hydride adduct. For the allyl anions X is hydrogen and the electrophilic partner is allene.

[c] Defined as the change in the C—O bond length of ketene which has occured at the transition state relative to that (larger) change which has occured in the adduct; % changes in the CH_2—C lengths and the O—C—C angles are qualitatively in the same order, that is, larger for perpendicular addition than for in-plane addition.

[d] Geometries were optimized at HF/6–311+G**. The C=O length in ketene is 1.136 Å at this level. See discussion in the text under Ketene.

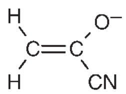
[e] These lengths are the C—C bond lengths the in allyl anions.

[f] This angle is the C—C—C angle in the allyl anions.

transition state are unstable toward departure of the isocyanide anion.

Three adducts of ketene with cyanide were investigated, the in-plane adduct, **1**(ad-ip), and two perpendicular adducts, **1**(ad-s-perp) and **1**(ad-a-perp). Perpendicular adduct **1**(ad-s-ip), having the lone pair on the pyramidal CH_2 group *syn* to the oxygen is more stable by 1.0–1.6 kcal mol^{-1} (1 kcal = 4.184 kJ) than the alternative adduct in which the lone pair is *anti* to the oxygen. The in-plane adduct is formed exothermically, $\Delta H_{\mathrm{ADD}} = -26.8$ kcal mol^{-1}, and is favored over the *syn* perpendicular adduct by 37.6 kcal mol^{-1} at the MP2/6–311+G** level.

The simplest reason for the large energetic difference between the in-plane and perpendicular adducts is that the former is an oxyanion enolate (the conjugate base of acetyl cyanide) while the latter is a primary carbanion with an attached acyl group unable to conjugate with the carbanion center. This conclusion is supported by computed (NPA) charges: the in-plane adduct has more negative charge on the oxygen than on C_β, whereas the opposite is true of the perpendicular adduct. To test this point further, two other systems were studied at the MP2/6–311+G** level. One was acetaldehyde enolate (**5**) and its perpendicular conformer (**6**). The latter species can be considered as the perpendicular hydride adduct of ketene, and as the transition state for rotation about the C—C bond of acetaldehyde enolate. For this process $\Delta H^{\ddagger} = 33.6$ kcal mol^{-1}, very similar to the difference between the in-plane and perpendicular cyano adducts of ketene. The second was allyl anion (**7**) and its perpendicular conformer (**8**). The activation energy for rotation about a C—C bond of the planar C_{2v} allyl anion via the perpendicular C_s transition state was found to be $\Delta H^{\ddagger} = 21.9$ kcal mol^{-1} (Foresman *et al.*[14] report a rotational barrier, $\Delta H^{\ddagger} = 20.9$ kcal mol^{-1} at the MP2/6–31+G* level). Although several factors are at work in determining the difference between this activation energy and the larger barriers found for the enolates, a dominant influence must be the ability of the enolates not merely to disperse negative charge but to relocate it to the highly electronegative oxygen atom.



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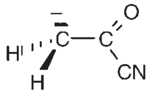

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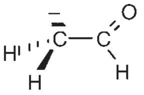

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Another view of these effects comes from consideration of the gas-phase acidities, ΔH_{ACID}, for propene and acetaldehyde. The computed values at the

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MP2/6–311+G** level are 390.0 and 367.5 kcal mol^{-1}, respectively, a difference of 22.5 kcal mol^{-1} favoring deprotonation of acetaldehyde (Experimental gas phase ΔH_{ACID} acid values range from 365.8 ± 2.2 to 366.5 ± 2.9 kcal mol^{-1} for acetaldehyde and from 389.1 ± 1.5 to 390.7 ± 2.1 kcal mol^{-1} for the allylic protons of propene[15]). For deprotonation to the perpendicular anions a smaller difference, $\Delta\Delta H_{\mathrm{ACID}} = 10.8$ kcal mol^{-1} is found. The larger $\Delta\Delta H_{\mathrm{ACID}}$ value arises from the difference between the combined resonance and polar effects of the formyl and vinyl groups whereas the smaller one may be attributed almost solely to the differential polar effects of the two groups. One may therefore infer that relative to the vinyl group, almost half the acid-strengthening ability of the formyl group is due to its polar effect.

Comparison of the in-plane and perpendicular adducts shows several interesting geometric features, listed in Table 3. Predictably, the C—O bond is shorter and the C_β—C_α bond longer in the perpendicular forms owing to the interruption of resonance. Likewise, one of the C—C bonds in the allyl anion lengthens while the other becomes shorter in the perpendicular form. Additionally the bond between the nucleophilic carbon in the CN moiety and the carbon to which it bonds is longer in the perpendicular adduct than in the in-plane adduct, a manifestation of negative hyperconjugation. This result is also seen in the perpendicular forms of acetaldehyde enolate and allyl anion in which the bond in question is the C—H bond at the central carbon. Finally, we note that the perpendicular anions are strongly pyramidalized at the anionic carbon. In fact the H—C—H angles are substantially less than 109.5°, especially in the ketene adducts. This implies additional p-character in the orbitals used to form the C—H bonds, thus additional s-character in the non-bonding orbital containing the lone pair, a stabilizing feature.

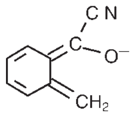
The transition state, **1**(ts-ip), for in-plane addition of cyanide to ketene is, by all measures, an early one, in agreement with Hammond's postulate. The distance between the nucleophilic and electrophilic carbons is very long: 0.74 Å longer than in the perpendicular transition state, **1**(ts-s-perp). Similarly, the fractional changes in several geometric features which have occurred at the ts, relative to the changes reached in the adducts, are much less for in-plane attack than for perpendicular attack (see Table 3).

Nucleophilic attack by isocyanide on ketene was also investigated, that is, attack by the nitrogen atom of CN$^-$ was examined. For in-plane attack the calculations converged normally both for adduct formation, **1**(ad-nc-ip), and for the corresponding transition state, **1**(ts-nc-ip). For perpendicular attack the calculations converged at the HF/6–311+G** level, but optimization at MP2 resulted in expulsion of the nucleophile. The MP2//HF ΔH values can considered only approximate; however, in-plane attack is heavily favored.

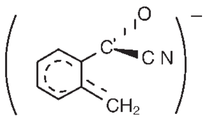
The reactions of isocyanide with ketene are not as exothermic as those using cyanide. The cyano in-plane adduct is 18.2 kcal mol^{-1} more stable than the isocyano in-plane adduct. However, the corresponding transition states differ by only 0.9 kcal mol^{-1}. A possible reason is that the structure obtained for the isocyano ts is a later one having a CN···C distance more than 0.5 Å shorter than in the cyano case, thus having more bonding character. As with attack by cyanide, the perpendicular geometry is strongly disfavored when isocyanide attacks.

6-Methylene-2,4-cyclohexadienylideneketene (6-MCDK)

Two adducts were calculated for the addition of cyanide to 6-MCDK (**2**). Both are formed exothermically. As shown in Table 2, the *anti* in-plane adduct, **2**(ad-a-ip), is more stable than the perpendicular adduct, **2**(ad-perp), by ca 20–21 kcal mol^{-1}. The alternative in-plane adduct with the cyano group *syn* to the methylene group did not converge.



2 (ad-a-ip)



2 (ad-perp)

Bond length alternation within the six-membered ring can be assessed from the average C—C lengths and the average deviation from this mean. Because not all structures could be optimized at the MP2/6–31+G* level, we used HF/6–31+G* geometries for this purpose. In the substrate the bond lengths within the ring vary from 1.331 to 1.471 Å. The average is 1.425 ± 0.062 Å, indicating a high degree of alternation. For the two adducts smaller ranges, smaller average lengths, and smaller average deviations are found. For the in-plane adduct the average C—C distance is 1.419 ± 0.049 Å, whereas for the perpendicular adduct it is 1.408 ± 0.031 Å. The latter nevertheless is not fully aromatized; the C—C distances in benzene at the HF/6–31+G* level are 1.388 Å.

Two transition states for the addition of cyanide to **2** were obtained, structures **2**(ts-a-ip), the *anti* in-plane ts, and **2**(ts-perp), the perpendicular ts. Calculation of a *syn* in-plane ts was not successful. As mentioned in Methods, calculation of the perpendicular structure required imposition of a constraint, and **2**(ts-perp) is therefore not a true transition state, but an approximation. It has two imaginary frequencies, one associated with the attack of cyanide and the other with rotation toward the in-plane geometry. The in-plane ts is about 7 kcal mol^{-1} more stable than the perpendicular ts.

Several geometric features show that the in-plane transition state is an earlier one than the perpendicular ts; see Table 4. The distance between the nucleophilic

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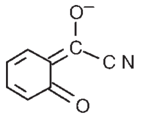
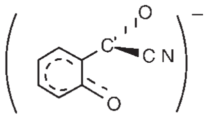
cyano carbon and the electrophilic ketene carbon in the more exothermic in-plane reaction is greater, 2.627 Å, than that for the perpendicular ts, 2.200 Å. The same conclusion is drawn from the distortion of the C=C=O angle at the ts: less for the in-plane structure. Some reduction of bond length alternation within the ring has already occurred in both transition states. Relative to the change in average C—C length which has occurred in the adducts, the reduction in average C—C length and the average deviation from the mean of this length are less for the in-plane than for the perpendicular ts, just as in the adducts.

6-Oxo-2,4-cyclohexadienylidineketene (6-OCDK)

Three cyano adducts were found for ketene **3**, the 6-oxoketene: two in-plane adducts, one of them with the cyano group *syn* to the 6-oxo group, **3**(ad-s-ip), and the other *anti*, **3**(ad-perp), plus a perpendicular form, **3**(ad-perp). Adduct formation is highly exothermic in all cases. Once again the ts structure found for perpendicular attack could be calculated only by constraining the attack angle to 90°. Once again, the structure found for the adduct has one imaginary frequency (rotation toward the in-plane geometry) whereas that for the transition state has two, the rotational motion plus the nucleophilic attack coordinate. Of the two in-plane adducts, the *syn* conformer is the more stable by 3.6 kcal mol^{-1}. This adduct is more stable than the perpendicular adduct by 9.6 kcal mol^{-1}, a smaller margin than for the 6-methyleneketene.



3 (ad-s-ip)



3 (ad-perp)

Two transition states were obtained for attack of cyanide on the 6-oxo ketene. Only an *anti* in-plane ts, **3**(ts-a-ip), was calculated; the *syn* in-plane ts input structure was not stable and converged to the *anti* structure. This structure has a single imaginary frequency, a very low frequency at −67 cm^{-1} corresponding to the addition reaction coordinate. The distance between the cyano carbon and the ketene carbon is very long, 2.64 Å, indicating a very early ts. The perpendicular ts, **3**(ts-perp), has two imaginary frequencies, one being the reaction coordinate and the other torsion toward the in-plane structure. The distance from the cyano carbon to the ketene carbon is shorter at 2.36 Å. The perpendicular ts is about 9 kcal mol^{-1} less stable than the in-plane ts, a

Table 4. Selected geometric features of 6-methylene-2,4-cyclohexadienylidineketene (**2**), 6-oxo-2,4-cyclohexadienylidineketene (**3**), 4-oxo-2,5-cyclohexadienylidineketene (**4**), their cyanide adducts and the corresponding transition states[a]

Compound	$d(C_{\alpha}—O)$ (Å)	$d(C_{\beta}—C_{\alpha})$ (Å)	d (C—CN) (Å)	$d(C{=}X)^{b}$ (Å)	Φ (O—C_{α}—C_{β}), (°)
2 6-MCDK	1.140 (1.179)	1.323 (1.342)	NA	1.335 (1.361)	179.9 (178.8)
2(ad-a-ip) (in-plane adduct, *anti*)	1.222 (1.270)	1.406 (1.423)	1.512 (1.485)	1.352 (1.380)	129.9 (128.1)
2(ad-perp) (perpendicular adduct)	1.190 (1.234)	1.481 (1.469)	1.512 (1.496)	1.371 (1.391)	128.6 (127.9)
2(ts-a-ip) (in-plane ts, *anti*)	1.136	1.351	2.627	1.345	159.4
2(ts-perp) (perpendicular ts)	1.140 (1.176)	1.391 (1.365)	2.200 (2.556)	1.350 (1.367)	150.7 (160.9)
3 6-OCDK	1.127 (1.167)	1.341 (1.353)	NA	1.208 (1.249)	179.3 (178.7)
3(ad-s-ip) (in-plane adduct, *syn*)	1.212 (1.254)	1.435 (1.440)	1.499 (1.486)	1.230 (1.270)	126.1 (126.1)
3(ad-a-ip) (in-plane adduct, *anti*)	1.200 (1.245)	1.438 (1.441)	1.523 (1.507)	1.225 (1.265)	131.0 (129.9)
3(ad-perp) (perpendicular adduct)	1.187 (1.232)	1.486 (1.475)	1.509 (1.493)	1.243 (1.281)	127.9 (126.8)
3(ts-a-ip) (in-plane ts, *anti*)	1.122	1.374	2.644	1.220	161.7
3(ts-perp) (perpendicular ts)	1.125	1.397	2.362	1.224	156.4
4 4-OCDK	1.135 (1.174)	1.329 (1.348)	NA	1.203 (1.249)	180.0 (180.0)
4(ad-ip) (in-plane adduct)	1.213 (1.256)	1.416 (1.429)	1.509 (1.491)	1.227 (1.269)	128.8 (128.0)
4(ad-perp) (perpendicular adduct)	1.190 (1.235)	1.479 (1.469)	1.508 (1.493)	1.242 (1.279)	128.1 (127.2)
4(ts-ip) (in-plane ts)	1.127 (1.167)	1.344 (1.362)	3.418 (3.196)	1.214 (1.259)	171.6 (168.0)
4(ts-perp) (perpendicular ts)	1.133 (1.173)	1.390 (1.387)	2.281 (2.313)	1.223 (1.264)	153.3 (154.9)

[a] Geometries were optimized at HF/6–31+G*; values in parentheses are those for optimization at MP2/6–31+G*.
[b] X is CH_2 for ketene **2** and O for ketenes **3** and **4**.

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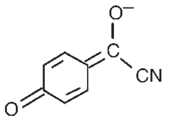
value similar to the difference between the calculated transition states for in-plane and perpendicular attack of cyanide on the 6-methyleneketene.

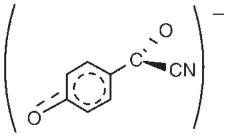
As expected, the geometry changes are smaller in the transition states than in the adducts. The 6-oxo C═O bond has lengthened, more so in the perpendicular ts than in the in-plane ts. Bond length alternation within the ring is greater for the transition states than for the adducts, and greater for the in-plane ts than for the perpendicular ts, again as expected.

4-Oxo-2,5-cyclohexadienylidineketene (4-OCDK)

Although experimental kinetic data on nucleophilic addition to 4-OCDK (**4**) have not been reported, a set of calculations was carried out for the nucleophilic addition of cyanide to this 4-oxo ketene, the 'para' isomer of the 6-oxoketene, **3**. At the MP2/6–31+G* level the in-plane adduct is more stable than the perpendicular adduct by 19.3 kcal mol^{-1}.



4 (ad-ip)



4 (ad-perp)

In-plane adduct formation is calculated to be more favorable for **4** than for **3** by 10 kcal mol^{-1}. This is because the 4-oxoketene is the less stable substrate (by 3.4 kcal mol^{-1}) and because its adduct is the *more* stable product (by 6.6 kcal mol^{-1}). It is interesting that the 6-oxoketene is more stable than its 4-oxo isomer in light of the fact that 1,2-benzoquinone is calculated to be *less* stable than 1,4-benzoquinone by 7.8 kcal mol^{-1}, also at MP2/6–31+G*. The superior stability of the 6-oxoketene is attributable to an attractive electrostatic interaction between the 6-oxo oxygen and C_α, the carbonyl carbon of the ketene moiety, an attraction sufficient to overcome van der Waals repulsion between the two atoms. [The 6-oxo oxygen and C_α are 2.71 Å apart in the ketene and 2.68 Å apart in the in-plane adduct. Computed charges (MP2/6–31+G*, NPA) are −0.59 for the oxygen and + 0.81 for C_α in the ketene changing to −0.68 and + 0.25 in the adduct. The group charge on the cyano moiety is − 0.10.] This interaction is, of course, absent in the 4-oxoketene. In 1,2-benzoquinone the corresponding interaction is a repulsive one between the two vicinal oxygen atoms. Geometric parameters support this statement. The distance and the intervening angles between the oxygens in 1,2-benzoquinone are larger than those between the 6-oxo oxygen and C_α in the ketene. Most striking is the distance between the ring carbons to which the oxygens in the quinone are attached: 1.549 Å, unusually long for a bond between two sp^2 carbons. In the ketene the corresponding C—C length is 1.481 Å. As for the adducts, the 6-oxo in-plane isomer shows the 6-oxo oxygen and C_α to be well within their combined van der Waals radii. This produces a repulsive interaction for which there is an insufficient compensating electrostatic attraction (see comment in square brackets above).

Perpendicular adduct formation is about as favorable for the 4-oxoketene as for the 6-oxoketene, a consequence of the fact that the 4-oxoketene and its perpendicular adduct are both less stable than their 6-oxo counterparts by similar amounts. The favorable electrostatic interaction between the 6-oxo oxygen and C_α, discussed above for the 6-oxoketene, also exists in its perpendicular adduct.

Activation enthalpies for the addition of cyanide to ketene **4** present a surprise. At the MP2/6–31+G* level the difference in $\Delta H^\ddagger$ for in-plane versus perpendicular attack is only 2.8 kcal mol^{-1}, favoring in-plane attack. At the MP2//HF level the difference has disappeared entirely. These small differences are a consequence of a greater activation enthalpy for in-plane attack and a smaller activation enthalpy for perpendicular attack for **4** relative to **3**. The result allows the possibility that for this ketene, perpendicular addition might compete with in-plane addition. A comparison between rates of nucleophilic addition to **4** (or 3,5-dimethyl-**4**) and the 2,6-dimethyl analog could settle the issue.

Charge distribution and bond length alternation in adducts of 2, 3 and 4

Adduct formation is more exothermic for the oxoketenes, **3** and **4**, than for the 6-methylene ketene, **2**. This is especially the case for the perpendicular adducts (Table 2). The electron-withdrawing power of the oxo substituent is the key. The NPA charge on the exocyclic CH_2 group is −0.080 in the in-plane adduct and −0.317 in the perpendicular adduct for ketene **2**. Ketenes **3** and **4** show greater negative charge at the exocyclic oxygens in their adducts: −0.67 for the in-plane adducts and −0.75 for the perpendicular adducts. In contrast, the amount of negative charge borne by the *ketenyl* oxygen of the adducts tends toward the opposite order: 6-methylene (in-plane) > 4-oxo (in-plane) ≥ 6-oxo (in-plane) > 6-methylene (perpendicular) ≈ 6-oxo (perpendicular) ≈ 4-oxo (perpendicular). The perpendicular adducts experience more delocalization of charge through the ring and into the exocyclic substituent than do the in-plane adducts.

The geometries are consistent with this picture. The lengthening of the exocyclic═CH_2 and═O bonds is distinctly greater for the perpendicular adducts of each ketene. Likewise, the perpendicular adducts have the shortest and the most similar bond distances between ring carbons indicating an increase in aromatic character. The average C—C distances between ring carbons for the adducts (HF/6–31+G* geometries) are 6-oxo (perp) = 1.405 ± 0.024; 4-oxo (perp) = 1.406 ± 0.026;

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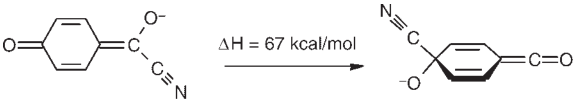
6-methylene (perp) = 1.408 ± 0.031; 4-oxo (in-plane) = 1.412 ± 0.039; 6-oxo (in-plane) = 1.414 ± 0.039; and 6-methylene (in-plane) = 1.419 ± 0.049 Å. Of course, the original ketenes have greater bond length alternation than their adducts with average C—C lengths of 1.425 ± 0.062, 1.420 ± 0.083 and 1.423 ± 0.059 Å for **2**, **3** and **4**, respectively. Hence all the evidence points to relatively greater aromatization for the perpendicular adducts of these ketenes, especially for **3** and **4**, than for the in-plane adducts. Even so, the in-plane products are favored in each case.

Although the degree of aromaticity attained by the perpendicular adducts of **2**, **3** and **4** is greater than for the in-plane adducts, it is noteworthy that reduced bond length alternation and some charge delocalization does occur in the in-plane adducts also. In-plane attack gives an enolate anion in which negative charge resides formally on the enolate oxygen. This oxygen formally has three lone pairs of valence electrons in orbitals at least one of which has π symmetry and is parallel to the vicinal $C_\alpha{=}C_\beta$ π system, hence with that of the ring. The MO thus produced is the HOMO-2 (with the remaining lone pairs occupying the HOMO and HOMO-1). By this interaction, conjugation with the ring and some back donation of electron density into the substituent at C6 (or C4) can be achieved (see Fig. 1).

Not only the adducts of ketenes **2**, **3** and **4**, but also the ketenes themselves may possess π systems with a measure of extra stability. This conclusion follows from a comparison between nucleophilic addition of cyanide anion to the 4-oxo carbonyl group of **4** and addition to the ketenyl carbonyl group; see Eqn (3). Addition of a nucleophile to the 4-oxo group disrupts the quinoid structure of the reactant and is calculated as thermoneutral at best—in contrast to the strongly exothermic addition to the ketene function.



4 (ad-ip) **4** (ad-oxo)

Bond length alternation in the transition states for 2, 3 and 4

The transition states for formation of both the in-plane and perpendicular adducts of ketenes **2**, **3** and **4** are early, especially the in-plane transition states. The HF/6–31+G* distances between the nucleophilic cyano carbon and the electrophilic ketenyl carbon in these cases range from 2.63 to 3.42 Å. For the perpendicular transition states these distances are shorter: 2.20 to 2.36 Å (see Table 4). Progress toward adduct geometry can also be inferred from the diminution of bond length alternation within the ring which has occurred at the transition states and the corresponding adducts, both relative to the original ketene. In all cases greater reduction of bond length alternation has occurred in the perpendicular transition states than for the in-plane adducts, just as expected from the nucleophile–electrophile distances cited above. It is interesting that the percentage reduction in the mean C—C bond lengths reached in the transition states, and also the reduction in the average deviation from that mean, is 50% or more except for the 4-oxo in-plane ts. If reduced bond length alternation is taken as a crude measure of an approach to aromaticity, one might infer that development of whatever aromatic character is possessed by the adducts is well along at the transition states, particularly the perpendicular ones, even though nucleophilic attachment is weak.

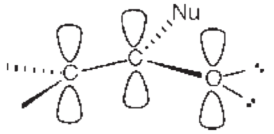


Figure 1. p-Orbital alignment allowing π-delocalization of negative charge for in-plane attack of a nucleophile on ketenes **2**, **3** and **4**

This point is of interest in view of Bernasconi *et al.*'s recent conclusion that in proton transfer reactions in which aromatic products are formed from non-aromatic precursors, development of aromaticity at the ts outpaces proton transfer.[16] Bernasconi *et al.*'s conclusion was based on experimental energetic considerations while the present results rely solely on computed bond lengths. While the agreement is intriguing, it cannot yet be regarded as anything more. Better ketene substrates for investigating this issue would be the cyclopentadienylideneketenes[17] in which the products of nucleophilic attack are fully aromatic.

CONCLUSIONS

In-plane attack of nucleophilic cyanide on ketene is strongly favored, both thermodynamically and kinetically, over perpendicular attack. The in-plane adduct is an enolate anion while the perpendicular adduct is a pyramidalized carbanion with an attached, orthogonal cyanocarbonyl group. The preference for in-plane attack holds also for the cyclic, conjugated ketenes 6-MCDK, 6-OCDK and 4-OCDK, despite an earlier prediction[5] that for the latter (and for the others by analogy) perpendicular attack might be likely. Nevertheless, the in-plane adducts of the cyclic, conjugated ketenes are not so strongly favored as for ketene itself, and calculated activation enthalpies indicate that perpendicular addition to 4-OCDK might compete kinetically.

The thermodynamic preference for in-plane over perpendicular addition, $\Delta\Delta H_{\mathrm{ADD}}$, decreases in the order ketene $\gg$ 6-MCDK $\geq$ 4-OCDK $>$ 6-OCDK. Reductions in C—C bond length alternation within the rings of the cyclic, perpendicular adducts occur in the same order, although the differences are not large. Hence there is indication of partial aromatization of the six-membered

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rings, greater for perpendicular addition than for in-plane addition of a nucleophile, and enhanced by the electron-accepting oxo substituent. Increased delocalization of negative charge (NPA) into the oxo group is also calculated for perpendicular attack in support of this argument.

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