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Structural, Spectroscopic, and Theoretical Study of 1-Acetylvinyl *p*-Nitrobenzoate, a Highly Reactive and Selective Captodative Olefin in Cycloaddition Reactions

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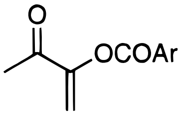
X-ray crystallography, variable temperature ^1H NMR and nuclear Overhauser effect experiments, and ab initio calculations provided evidence of the *s-trans* preferential conformation of captodative olefin 1-acetylvinyl *p*-nitrobenzoate (**1a**) in solid, solution, and gas phases. The reactivity of **1a** in cycloaddition reactions was rationalized under the basis of experimental ionization energy and electron affinity parameters. Correlation of the latter with the frontier molecular orbitals, calculated at the ab initio 3-21G and 6-31G* levels, suggests a nonsignificant effect of the electron-donor group upon control of the reactivity and regioselectivity of these olefins in Diels−Alder reactions.

1. Introduction

Pericyclic cycloaddition reactions have been traditionally considered as powerful tools in assessing the structural and electronic factors that control chemical reactivity and selectivity in any concerted organic process.[1] In particular, Diels−Alder and 1,3-dipolar cycloadditions have been invaluable synthetic reactions in the preparation of complex organic molecules.[2]

Due to the opposite electronic demand displayed by their geminally substituted functional groups, captodative olefins have attracted special attention in recent years.[3] We have shown that 1-acetylvinyl *p*-nitrobenzoate (**1a**), among other analogous olefins, **1b**−**1e**, was highly reactive and selective in Diels−Alder[4] and 1,3-dipolar cycloadditions,[5] and it also proved to be a very useful synthon in natural product synthesis.[6]



1a, Ar = C_6H_4*p*-NO_2
1b, Ar = α-naphthyl
1c, Ar = β-naphthyl
1d, Ar = phenyl
1e, Ar = C_6H_3-2,4-$(NO_2)_2$

The reactivity and selectivity shown in Diels−Alder additions by these captodative olefins have been rationalized in terms of frontier molecular orbital (FMO) theory.[4a] Preliminary ab initio STO-3G and MINDO/3 calculations of olefins **1** suggested that these dienophiles react under conditions of *normal electronic demand* (NED) in Diels−Alder reactions with dienes substituted with electron-donating groups. However, in the presence of dienes monosubstituted with electron-withdrawing groups, both HOMO-diene/LUMO-dienophile and LUMO-diene/HOMO-dienophile (*inverse electronic demand*, IED) interactions would be involved. Coefficient differences of the proper frontier molecular interaction between diene and dienophile were estimated in order to predict regioselectivity. Secondary orbital interactions were also invoked as an attempt to explain the selectivity observed with deactivated dienes.[4a]

It has been suggested that in Diels−Alder reactions, the *cisoid*−*transoid* conformational equilibrium of the dienophile may have an important steric effect, directing the approach of the diene at the transition state. The effect is expected to be more important when the cycloadditions are promoted by Lewis acids.[7] MINDO/3 calculations provided information about the conformational stability of olefin **1a**, the *s-cis* conformation being more stable than the *s-trans* by ca. 2.0 kcal/mol. From the perturbational model point of view, the addition of electron-donating groups to the double bond of the olefin gives rise to a destabilization of the highest occupied molecular orbital (HOMO). On the other hand, the introduction of an electron-withdrawing group on the ethylene produces, as expected, the opposite effect. As an extension of Koopmans' theorem,[8] the perturbation of the π_{CC} HOMO orbital by the substituents should be reflected in the ionization energies (IEs).[9] Indeed, whereas $IE_{ethylene} = 10.52$ eV (π_{CC}), the IEs of vinyl acetate and methyl acrylate are 9.85 eV[10] and 10.72 eV,[11] respectively. The electron-demand effect of the substituent on the HOMOs linearly correlates with the lowest unoccupied molecular orbital (LUMO) energies: both LUMO and HOMO will be stabilized, for example, as a result of increasing the number of electron-withdrawing groups in the double bond.[9] This correlation should be reflected in the electron affinities (EAs) and IE values of the molecule.[12]

With the aim of elucidating the structural and electronic factors which provide the distinctly high reactivity and selectivity of captodative olefins **1**, in particular of olefin **1a**, in cycloaddition reactions, we undertook an extensive study of this molecule. Electron transmission (ET) and ultraviolet photoelectron (UP) spectroscopies, X-ray diffraction, variable temperature ^1H NMR and nuclear Overhauser effect (NOE) experiments, and ab initio (RHF/3-21G and 6-31G*) calculations of **1a** were carried out. The results are described in the present report.

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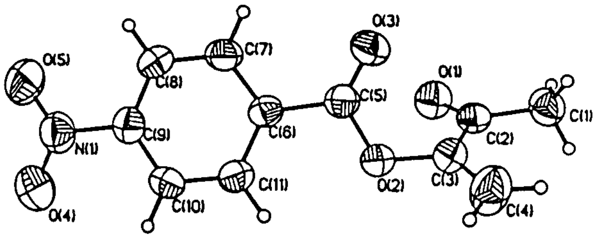


Figure 1. ORTEP structure of **1a**.

TABLE 1: Crystal Data for Compound 1a

formula	$C_{11}H_9NO_5$
Mw (g mol^{-1})	235.19
crystal system	monoclinic
space group	P-2_1
crystal size (mm)	0.2 × 0.25 × 0.35
a (Å)	6.2080(10)
b (Å)	12.990(2)
c (Å)	6.7730(10)
β (deg)	91.810(10)
V (Å^3)	545.9(2)
Z	2
F(000)	244
radiation	Mo Kα
μ (mm^{-1})	0.115
D_c (g cm^{-3})	1.431
scan type	$2\theta/\theta$
2θ scan range (deg)	45
θ limits (deg)	3.01−22.49
temperature	25 °C
no. of reflections collected	1086
no. of unique reflections collected	827
no. of unique observed reflections	747
R	0.039
R_w	0.0877
goodness of fit, s	1.042
largest residual peak (e Å^{-3})	0.127

2. Results and Discussion

2.1. X-ray and Variable Temperature NMR Experiments. The optimized preparation of compound **1a**[6b] yields pale-yellow crystals, which after slow recrystallization from hexane/EtOAc (9:1) produced single translucent crystals. A crystallographic analysis of **1a** was carried out in order to establish the conformation of the enone system in the solid state. The X-ray structure is illustrated in Figure 1, and crystallographic data are summarized in Table 1. Selected bond distances, bond angles, and torsion angles are collected in Table 2. The enone system appears in a conjugated planar *s-trans* conformation, with the *p*-nitrobenzoyl group out of the plane formed by the enone π system; the carbonyl ester group and aryl ring are also conjugated. This conformation is similar to those of trisubstituted analogous olefins.[13] Deviations of the planarity for the enone and the *p*-nitrobenzoyl moieties are determined from the torsion angles: C(4)−C(3)−C(2)−C(1) = −8.9° and C(7)−C(6)−C(5)−O(3) = 11.9°.

TABLE 2: Selected Interatomic Distances (angstroms), Bond Angles (deg), and Torsion Angles (deg) (Estimated Standard Deviations) of the Crystal Structure of 1a

Bond Distances

C(1)−C(2)	1.494(5)
C(2)−O(1)	1.215(5)
C(2)−C(3)	1.490(5)
C(3)−C(4)	1.306(6)
C(3)−O(2)	1.398(4)
C(5)−O(3)	1.200(4)
C(5)−O(2)	1.353(4)
C(5)−C(6)	1.488(5)
C(6)−C(11)	1.389(4)
C(6)−C(7)	1.391(5)
C(7)−C(8)	1.380(5)
C(8)−C(9)	1.373(5)
C(9)−C(10)	1.373(5)
C(9)−N(1)	1.475(5)
C(10)−C(11)	1.371(5)
N(1)−O(4)	1.206(4)
N(1)−O(5)	1.217(4)

Bond Angles

O(1)−C(2)−C(3)	119.3(3)
O(1)−C(2)−C(1)	121.9(4)
C(3)−C(2)−C(1)	118.7(4)
C(4)−C(3)−O(2)	118.5(4)
C(4)−C(3)−C(2)	126.7(4)
O(2)−C(3)−C(2)	114.6(3)
O(3)−C(5)−O(2)	123.0(3)
O(3)−C(5)−C(6)	125.2(3)
O(2)−C(5)−C(6)	111.8(3)
C(10)−C(11)−C(6)	120.1(3)
C(11)−C(6)−C(5)	122.1(3)
C(7)−C(6)−C(5)	117.8(3)
C(8)−C(7)−C(6)	119.6(3)
C(9)−C(8)−C(7)	119.0(3)
C(10)−C(9)−C(8)	122.1(3)
C(10)−C(9)−N(1)	119.0(3)
C(8)−C(9)−N(1)	118.9(3)
C(11)−C(10)−C(9)	119.0(3)
C(11)−C(6)−C(7)	120.1(3)
O(4)−N(1)−O(5)	123.4(4)
O(4)−N(1)−C(9)	119.1(3)
O(5)−N(1)−C(9)	117.4(3)
C(5)−O(2)−C(3)	116.7(2)

Torsion Angles

C(4)−C(3)−C(2)−O(1)	170.3	171.2[a]
C(4)−C(3)−C(2)−C(1)	−8.9	−8.3
H(4a)−C(4)−C(3)−C(2)	−173.9	−178.2
H(4b)−C(4)−C(3)−C(2)	6.1	1.4
C(5)−O(2)−C(3)−C(4)	116.2	113.8
C(5)−O(2)−C(3)−C(2)	−69.1	−70.7
O(3)−C(5)−O(2)−C(3)	−5.6	−10.8
C(7)−C(6)−C(5)−O(2)	−167.4	175.5
C(11)−C(6)−C(5)−O(2)	−12.1	−5.2
C(7)−C(6)−C(5)−O(3)	11.9	−3.1
C(11)−C(6)−C(5)−O(3)	−168.6	176.6
H(7)−C(7)−C(6)−C(5)	−1.4	0.1
H(11)−C(11)−C(6)−C(5)	0.2	−0.2
C(2)−C(3)−O(2)−C(4)	174.7	175.4
C(7)−C(11)−C(3)−C(2)[b]	−60.2	−81.5
C(7)−C(11)−C(3)−C(4)[b]	127.0	108.1

[a] The data presented in this column are from the calculated 6-31G* nonplanar *s-trans* structure of **1a**. [b] It can be considered as the dihedral angle between the enone and benzoate planes.

Variable temperature ^{1}H NMR and NOE experiments were carried out in order to determine the conformation of the enone π system of **1a** in solution. A deuteriochloroform solution of **1a** was cooled, and NOE difference spectra were recorded at five temperatures: 21, −20, −30, −40, and −50 °C. The signals of the methyl group and the (*E*)-vinyl proton were irradiated, and the enhancements were calculated for the rest of the signals (Table 3). A single NOE enhancement between these protons was detected (Figure 2, structure I). No significant NOE enhancement was observed with the aromatic protons. This could be explained as a consequence of the rotational restrictions of the benzoyloxy group at these temperatures. Probably in the most stable conformation, the aromatic protons lie far from the enone π system, avoiding the approach to the methyl group as would be the case for structure II (Figure 2).

We can conclude that the NOE experiments provide evidence of the presence of the *s-trans* conformation I in solution. However, they are unable to rule out the *s-cis* conformer III. Indeed, the contribution of the *s-cis* isomer to the conformational equilibrium could not be estimated by this means. No doubling of the signals was observed and the chemical shifts did not

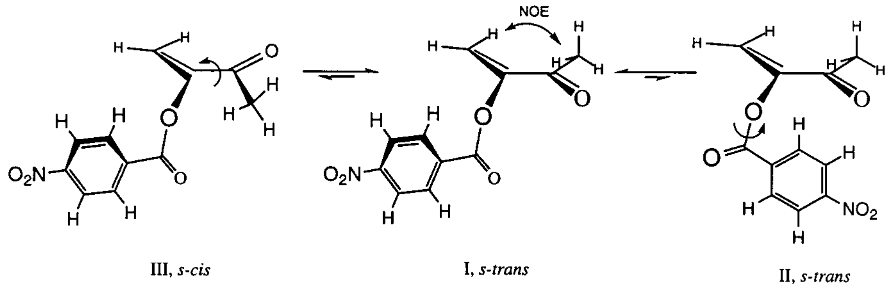
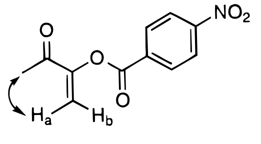


Figure 2. Probable conformational equilibria of **1a**.

TABLE 3: Relative NOE Enhancements (percent) Calculated at Several Temperatures for Olefin 1a

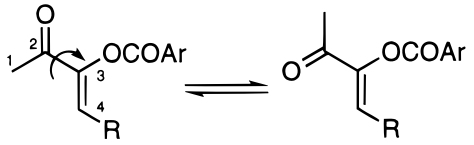


1a

T (°C)	NOE (%)	
	{CH$_3$} H$_a$	{H$_a$} CH$_3$
21	2.6	2.5
−20	4.5	2.0
−30	3.7	2.3
−40	5.0	1.0
−50	5.0	1.8

change significantly, as would be expected for the methyl group and the (*E*)-proton signals.[13a] In addition, the ^{1}H NMR spectrum of **1a** did not change at higher temperatures (75 °C, DMSO-d_6).

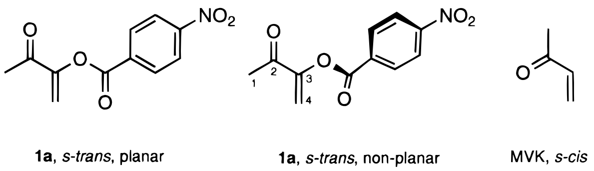
If one compares the above results to those observed for analogous systems such as **2a**, in which a barrier of 14.0 kcal/mol was determined by ^{1}H NMR for the *s-cis/s-trans* rotation (coalescence temperature of 18 °C),[13a] it is likely that the energy barrier would be less than 11.0 kcal/mol for **1a**. A strong electron-releasing effect of the lone pair of the nitrogen atom through the enone π system was invoked in order to explain the rotational barrier of **2a**. This effect was further supported by the shortening of the C$_4$−N (1.32(1) Å) and C$_2$−C$_3$ (1.41(1) Å) bonds observed in the X-ray structure. The bond distances for C$_2$−C$_3$ in **1a** (1.490(5) Å) and in the related compound **2b** (1.50(4) Å)[13b] are longer than that in **2a**, suggesting a lower rotational barrier for the former, as shown by the variable temperature NMR experiments.



2a, R = NMe$_2$
2b, R = Me
Ar = C$_6$H$_4$*p*-NO$_2$

Although these facts do not preclude the presence of the *s-cis* conformer, the *s-trans* isomer appears to be the major one at equilibrium in solution, inasmuch as it is the only one obtained by recrystallization, as shown by the X-ray structure (Figure 1). Moreover, the energies of both rotamers of **1a** were calculated at the ab initio RHF/3-21G and 6-31G* levels (vide infra); the nonplanar *s-trans* was found to be the most stable at the highest level (Table 4).

TABLE 4: Ab Initio Energies (au) of the Minimum-Energy Conformations of Olefins 1a and MVK and Relative Stabilities



compound	conformation	method	E	relative stability (kcal/mol)[a]
1a	*s-cis*, planar	3-21G	−845.645 667	−3.80
1a	*s-trans*, planar	3-21G	−845.641 866	−1.40
1a	*s-cis*, nonplanar	3-21G	−845.642 534	−1.80
1a	*s-trans*, nonplanar	3-21G	−845.639 649	0.00
1a	*s-cis*, planar	6-31G*	−850.428 953	2.20
1a	*s-trans*, planar	6-31G*	−850.429 046	2.10
1a	*s-cis*, nonplanar	6-31G*	−850.431 177	0.80
1a	*s-trans*, nonplanar	6-31G*	−850.432 446	0.00
MVK	*s-cis*, planar	3-21G	−228.522 041	0.00
MVK	*s-trans*, planar	3-21G	−228.518 929	1.95
MVK	*s-cis*, planar	6-31G*	−229.806 306	0.00
MVK	*s-trans*, planar	6-31G*	−229.805 907	0.25

[a] Considered per each compound and method series.

2.2. Photoelectron and Electron Transmission Spectroscopies of 1a and Related Molecules. UP spectroscopy has provided a wealth of information about the IEs, which can be equated, assuming the validity of Koopmans' theorem, to the negative of the energies of the filled molecular orbitals (MOs). As a complement to this technique, ET spectroscopy[14] provides the corresponding information about the normally unoccupied MOs. ET spectroscopy measures the energies (attachment energies, AEs) at which electrons are temporarily captured into empty orbitals. This process is referred to as shape resonance, and the measured AE values can be equated to the negative of the vertical EA values. The most serious limitation of the ET spectroscopy technique is that formation of stable anion states cannot be detected, and therefore positive EA values cannot be measured. These experimental techniques, together with ab initio calculations, were employed to provide a description of the FMOs in **1a**.

The He(I) UP spectra of **1a** and, for comparison, methyl *p*-nitrobenzoate (MNB) and methyl vinyl ketone (MVK) are shown in Figure 3. For the former two compounds, the spectra show broad overlapping bands for which a clear and decisive assignment of contributions from the various orbitals is not possible. However, by comparing the spectra with those of related compounds and taking into account the relative intensities of the bands, the outermost orbitals of **1a** can be assigned as follows.

The spectrum of MVK is the same as that previously reported.[11] The first three ionizations are assigned to the n_O (oxygen lone pair), ethylenic π_{CC} and π_{CO} MOs, respectively

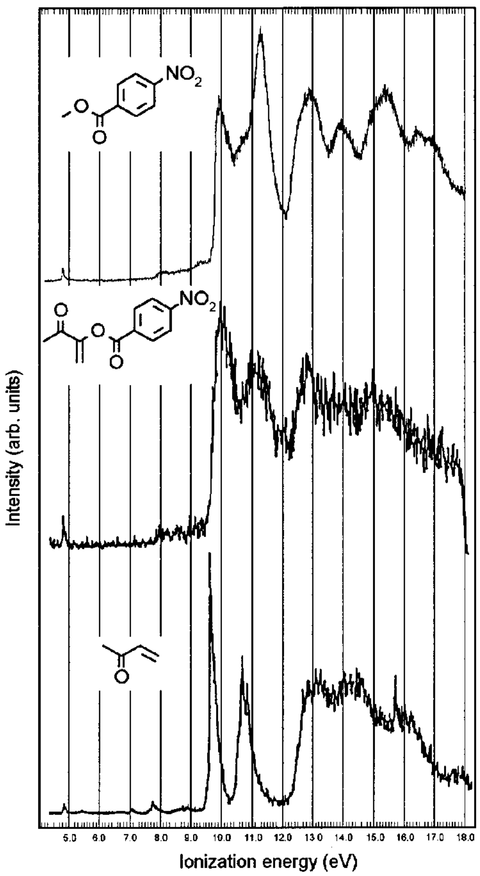


Figure 3. UP spectra of **1a**, MNB, and MVK.

TABLE 5: Ionization Energies (eV) and Electron Affinities (eV) of Ethylene, 1a, MVK, MNB, and Isoprene (3) Corresponding to MOs

compound	IE	EA
ethylene	10.51[a] (10.52)[b]	−1.73[c]
1a[d]	10.1, 11.2	−2.04, −4.40
MVK[d]	9.60 (9.61)[e]	−2.93
MNB[d]	10.05, 11.35	−2.27, −4.30
3[a]	8.85, 10.90	

[a] Reference 17. [b] Reference 9. [c] Reference 19. [d] This work. [e] Reference 11.

(Table 5). The spectrum of MNB, compared to that of nitrobenzene, shows the presence of two additional oxygen lone pair ionizations. The first band, peaking at slightly above 10 eV, is assigned to the ring π_S and π_A orbitals as in nitrobenzene (Scheme 1). The second band, with a leading shoulder at 10.8 eV attributed to $n_{o(C=O)}$ (10.2 eV in methyl benzoate[15]), peaking at 11.35 eV also comprises ionization from the methoxy lone pair, $n_o(\pi)$ (10.9 eV in methyl benzoate[15]), and the outermost σ and π orbitals of the nitro group (11.15 and 11.31 eV in nitrobenzene[16]). The intensity of the first band, relative to the total intensity of the second, is approximately 2:4, thus accounting for the ionizations of the six assigned orbitals.

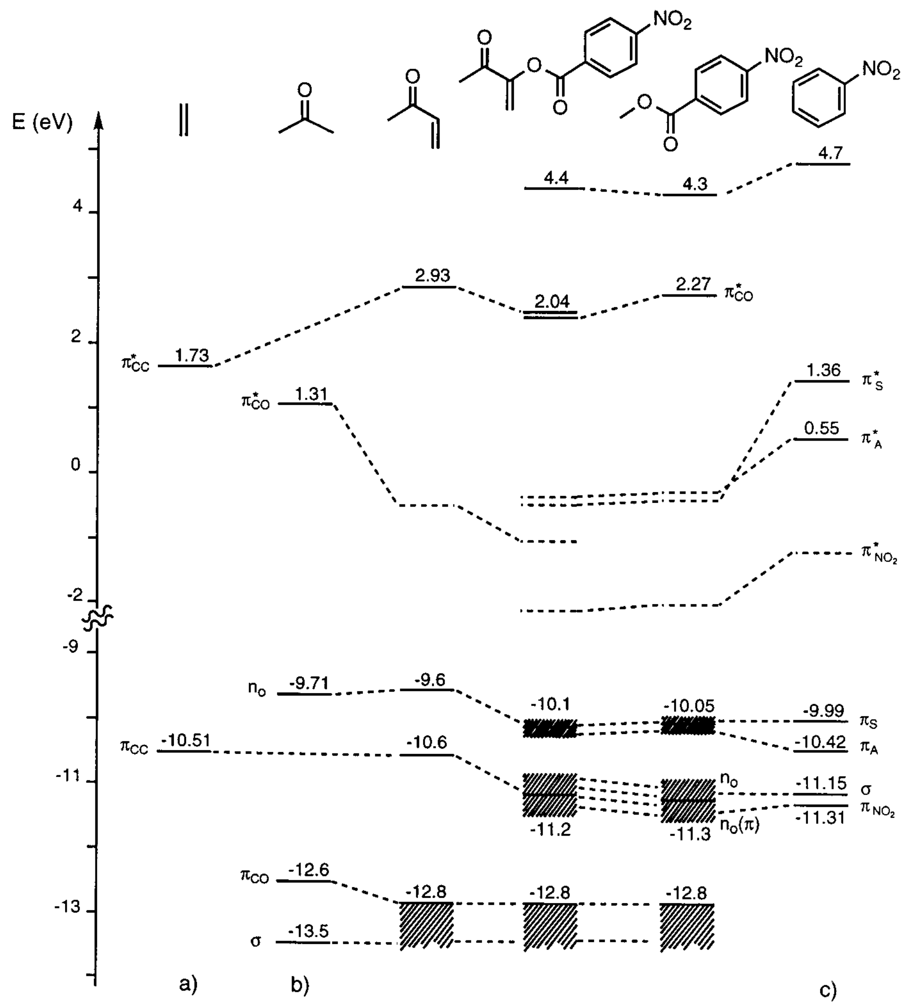
The first two bands in the UP spectrum of **1a** (Figure 3) centered at 10.1 and 11.2 eV are assigned to ionizations of the eight highest occupied orbitals. The first band at 10.1 eV is due to ionization from the following MOs: n_o, the oxygen lone pair of the enone moiety (9.61 eV in MVK[11]), and the ring π_S and π_A orbitals (9.99 and 10.42 eV in nitrobenzene[16]). The second broader band contains contributions from the ionization of the $n_{o(C=O)}$ ester frame, the ethylenic π_{CC} (10.6 eV in MVK), the outermost σ and π of the nitro group (11.15 and 11.31 eV in nitrobenzene[16]), and n_o, the lone pair of the “bridging” oxygen atom of the ester. Using approximate measurements of the areas under the bands, the intensity of the first band, relative to the second broader one, is 3:5. The σ and π MOs corresponding to the third and fourth HOMOs in benzene are expected under the broad band centered at 12.8 eV, together with the π_{CO} MOs of the enone and PNB moieties, followed by the σ MOs of the molecular skeleton. The ionization energy of ethylenic π_{CC} orbital in **1a** (11.2 eV) should thus be greater than that in MVK (10.6 eV), due to the overall inductive effect of the PNB portion of the molecule on the enone moiety.

The ET spectrum of MVK, MNB and **1a** are displayed in Figure 4. The ET spectrum of MVK shows a single resonance, centered at 2.93 eV. Strong mixing between the (close-in-energy) empty π^*_{CO} and π^*_{CC} group orbitals (AE = 1.31 eV in acetone[18] and 1.73 eV in ethene,[19] respectively, see Scheme 1) gives rise to two π^* MOs in MVK. It is to be noted that these two orbitals are delocalized over the C=C and C=O double bonds. The resonance observed at 2.93 eV is therefore associated with the out-of-plane combination of the π^*_{CO} and π^*_{CC} group orbitals. Considering the energy shift (1.2 eV) of this MO, with respect to the π^*_{CC} resonance in ethene and the electron-withdrawing inductive effect of the carbonyl group, the in-phase counterpart (i.e., the LUMO of MVK) is expected to lie at least 1.2 eV lower in energy than the π^*_{CO} in acetone, that is, close to or below zero energy. The absence of a low-energy resonance in the ET spectrum confirms this prediction and indicates that electron capture into the LUMO gives rise to a stable anion state (thus not detectable in ETS), hence MVK possesses a positive EA. As a limiting case, the resonance associated with the LUMO could occur just slightly above zero energy, where it would be masked by the intense electron beam signal.

In going from nitrobenzene to MNB, the LUMO (with mainly π^*_{NO2} character) is expected to be stabilized, because of mixing with the additional empty π^*_{CO} orbital and the stabilizing inductive effect of the carbonyl group. Consistently, nitrobenzene possesses a positive EA of 1.0 eV,[20] while the EA of *p*-nitrobenzoic acid was evaluated to be 1.84 eV[21] by means of HAM/3 calculations, in agreement with voltammetry data. Analogous considerations, and mainly owing to the proximity in energy between the interacting group orbitals, suggest that the symmetric ring orbital of MNB (labeled π^*_S in Scheme 1, AE = 1.36 eV in nitrobenzene[22]) must be strongly stabilized by the carbonyl substituent in the *para* position. The antisymmetric counterpart (π^*_A, 0.55 eV in nitrobenzene) is only inductively stabilized. These two MOs are therefore expected to lie close to or below zero energy in MNB. The remaining two empty orbitals of the latter, in order of increasing energy, are mainly the ester π^*_{CO} orbital (also possessing ring and NO_2 π^* character) and the highest-lying benzene π^* orbital (4.82 eV in benzene[23]). Electron capture in the latter MO accounts for the resonance displayed at 4.3 eV in the ET spectrum of MNB, indicating that the prevailing effect of the carbonyl group in this ring orbital is an inductive stabilization. The only other resonance observed in the spectrum (2.27 eV) is associated with the π^*_{CO} orbital. The absence of resonances at lower energy implies that the first three anion states are stable (or, as a limiting case, very close to zero energy), as qualitatively represented in Scheme 1.

The empty-level MO structure of **1a** can be imagined as the sum of the π^* systems of the MVK and *p*-nitrobenzoyl moieties, separated by an oxygen atom and far from coplanarity. The ET spectrum of **1a** is similar to that of MNB. The highest-lying resonance (4.4 eV) correlates with the 4.3 eV resonance of MNB. The resonance centered at 2.04 eV is assigned to the

SCHEME 1: Correlation Diagram for the FMO Energies in 1A, MNB, MVK, and Related Molecules, As Deduced from UP and ET Spectroscopies[a]



[a] The energy position of the empty levels close to or below zero energy, represented by dashed lines, are only tentative (see text). The UP and ET spectroscopy data are taken from (a) refs 17 and 19, (b) refs 15 and 18, and (c) refs 16 and 22.

unresolved contributions of the π^*_{CO} MO of PNB and of the second π^* MO of the MVK moiety. The relatively large width (1.0 eV) of this resonance when compared to that (0.70 eV) of the corresponding resonance located at 2.27 eV in MNB is in agreement with the presence of two unresolved signals. It can be noted that the second π^* MO of MVK (out-of-plane π^*_{CO}/π^*_{CC} combination, AE = 2.93 eV) is stabilized by the PNB substituent in **1a**, even though mixing with an oxygen lone pair can cause a large destabilization of adjacent empty π^* orbitals.[18] This stabilization can be explained in terms of the conformation of **1a**, in which the overlap between the oxygen lone pair and the enone π^* system is largely reduced (see structural data below), and of a strong inductive (−I) effect of the PNB substituent. This finding suggests that the in-phase π^* counterpart should also be stabilized in going from MVK to **1a**.

2.3. Ab Initio Calculations. Frontier molecular orbital theory has been a useful treatment in the study of reactivity. It assumes that the energies and shapes of the HOMOs and LUMOs of the addends dictate the outcome in concerted cycloadditions.[24,25] Other models have been proposed to account for the observed regiochemistry of substituted dienes and olefins.[26] Both, these models and the FMO theory, predict the correct orientation in additions of monosubstituted olefins and dienes.[27] As mentioned earlier, Koopmans' theorem allows one to equate the energy of the FMOs to the IEs and EAs of a

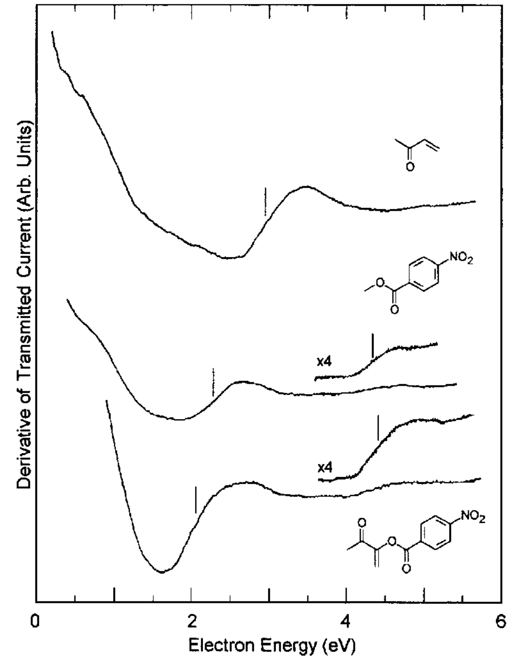
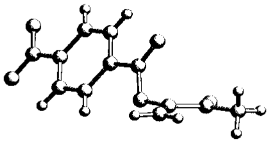


Figure 4. ET spectra of **1a**, MNB, and MVK. Vertical lines locate the most probable vertical AE values.

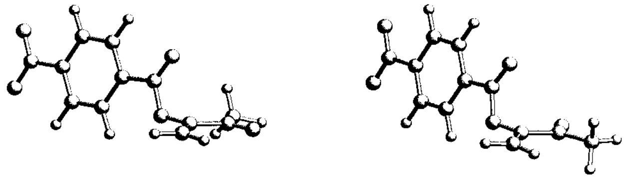
TABLE 6: Ab Initio RHF/3-21G and 6-31G* Frontier Molecular Orbitals of Olefins 1a, MVK, and Isoprene (3)

		3.21G	6.31G*
compound	FMO	*E* (eV)	*E* (eV)
1a[a]	HOMO[b]	−11.0460	−11.0123
	LUMO[c]	2.2417	2.4588
MVK[d]	HOMO	−10.5391	−10.4895
	LUMO	2.9002	2.9222
3	HOMO	−8.7107	−8.6193
	LUMO	3.5451	3.5337

[a] Of the nonplanar *s-trans* conformation. [b] The energies correspond to the 2NHOMO, since its HOMO and NHOMO do not have a p_z contribution. [c] The energies correspond to the NLUMO, since its LUMO does not have p_z contribution. [d] Of the most stable *s-cis* conformation.

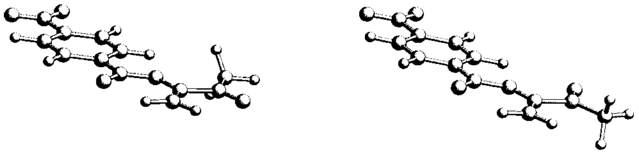


X-ray



non-planar, *s-cis*
(-850.431177 a.u.)

non-planar, *s-trans*
(-850.432446 a.u.)



planar, *s-cis*
(-850.428953 a.u.)

planar, *s-trans*
(-850.429046 a.u.)

Figure 5. Perspective view and energies of the X-ray crystal and calculated (6-31G*) structures of **1a**.

molecule,[8] resulting in good agreement between theoretical and experimental results.[9]

Ab initio 3-21G and 6-31G* calculated energies and FMOs of olefin **1a** and MVK are listed in Tables 4 and 6. The nonplanar and planar (with respect to the enone and PNB moieties) *s-trans* conformers are more stable than the *s-cis* in captodative olefin **1a** at the 6-31G* level (Table 4). However, the *s-cis* conformer is more stable in both nonplanar and planar conformations in the 3-21G calculation. On the other hand, in MVK, the *s-cis* conformer is the most stable. Interestingly, the structure of **1a** found to be the most stable by the 6-31G* calculations was almost identical with the X-ray structure (Figure 5). A good correlation can be found between experimental IEs and calculated HOMOs of both olefins. In addition, the relative energies of the LUMOs seem to be in agreement with the relative EAs determined for MVK and olefin **1a**, with the experimental LUMO energy of the latter probably being more stable than that of the former.

The reactivity of a series of analogous dienophiles in Diels−Alder reactions has been associated to the EAs.[9] Thus, considering a common diene, the higher the EA, the more reactive the olefin. This occurs when the olefin is substituted by electron-withdrawing groups. An analogous correlation can be done with the LUMOs of the olefins. From the data listed in Tables 5 and 6, it is apparent that **1a** should be more reactive than MVK; nevertheless, the kinetic data have shown that MVK is about 2.6 times more reactive than **1a**.[28] This opposite reactivity could be attributed to steric hindrance, which is expected to be more significant in **1a**.[29]

The slight difference in reactivity is rather surprising, considering that olefin **1a** possesses an electron-releasing group, which is expected to decrease the rate of cycloaddition[24] by raising both HOMO and LUMO energies.[9] Therefore, it appears that the effect exerted by the oxygen of the aroyloxy group is not that of a strong electron-donor group. This is probably accounted for by the presence of factors such as (a) inefficient overlap of the lone pairs of the "bridging" oxygen atom upon the π_{CC} MO of the olefin and (b) an inductive effect from the aroyloxy group, which would give rise to an stabilizing overall effect on the LUMO of olefin **1a**: olefin **1e**, which bears two nitro groups in the aromatic ring, is almost as reactive as MVK.[28]

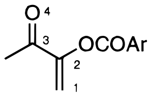
The first hypothesis is supported by the fact that there is no significant contribution of the oxygen ($C < 0.025$) to the lowest five empty orbitals with π^*_{CC} character of **1a**. In contrast, a more important oxygen coefficient ($C = 0.1816$) is present in the 2NHOMO, with π_{CC} character. This would explain the facts that **1a** has a more stable HOMO than MVK, as anticipated by the UP spectrum, and that the coefficient on the unsubstituted carbon C-1 is larger than in the geminally substituted C-2 (Table 7). Apparently, the partial inhibition of resonance, between the lone pairs of the oxygen and the π_{CC} of the double bond, would be facilitated by a conformational restriction and by a delocalization of the electronic density through the π_{CO} MO of the *p*-nitrobenzoyloxy (PNB) carbonyl group. Indeed, when the contribution of the latter is important to the empty orbitals, moderate size ($C < 0.089$) coefficients of the oxygen atom orbitals are found.

It is likely that repulsive van der Waals interactions, created between the PNB group and the planar enone system, would oblige the former to acquire an almost perpendicular and restricted conformation. The X-ray structure shows a dihedral angle between the mean plane through the PNB group with respect to the π enone moiety of 127.0°. In this preferential conformation, the lone pairs of oxygen are not coplanar to the π orbital of the double bond, decreasing the possibility of overlapping. Bond distances in the X-ray structure of **1a** (Figure 1) would reveal this lack of electron delocalization, by showing a lengthening of the $C_3{-}O_2$ bond. Indeed, the bond length (1.398(4) Å, Table 2) is longer than the average values for a delocalized $C{=}\mathbf{C}{-}\mathbf{O}{-}CO$ bond in esters (1.353 Å).[30] Even longer $C_3{-}O_2$ bonds have been determined (>1.42 Å) for β-substituted analogues of **1a**.[13] Moreover, a competitive and more efficient delocalization of the lone pairs of oxygen toward the carbonyl group of the ester would be in agreement with the fact that the bond distance for the $C_5{-}O_2$ bond (1.353(4) Å) is within the average values for a vinyl ester (1.359 Å).[30]

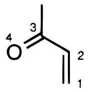
This fact is highly relevant if this conformation is maintained at the transition states of the Diels−Alder or 1,3-dipolar additions, since the electron-donor effect of the PNB group will be partially inhibited. Therefore, the reactivity of captodative olefins **1** in cycloaddition reactions is controlled to a large extent by the acetyl group and by the electron-withdrawing inductive effect of the aroyloxy group. From the FMO point of view, this effect will produce a stabilization of the LUMO of the olefin and, consequently, will increase the reactivity and selectivity of the cycloaddition.[24]

Thus, the stabilization of the LUMO, due to the aforementioned factors, would rationalize the high reactivity of olefin **1a** in Diels−Alder reactions and, by extension, of all the captodative olefins acetyl vinyl arenecarboxylates **1**.[28] Additional factors, such as the captodative effect[31] or steric

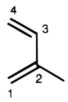
TABLE 7: Ab Initio 3-21G and 6-31G* Calculations of Energies (eV) and Coefficients (C_i) of the Frontier Molecular Orbitals of Olefins 1a, MVK, and Diene 3[a]



1a, Ar = $C_6H_4p\text{-}NO_2$



MVK



3

		HOMO[b]					LUMO[c]				
compd[d]	level	C_1	C_2	C_3	C4	ΔC_i[e]	C_1	C_2	C_3	C4	ΔC_i[e]
1a	3-21G	−0.2991	−0.2873	0.0326	0.1516	0.0118	0.2548	−0.1972	−0.2507	0.2474	0.0576
	6-31G*	−0.3593	−0.3565	0.0236	0.1676	0.0028	0.2940	−0.2386	−0.2889	0.2800	0.0554
MVK	3-21G	0.2935	0.3031	−0.0519	−0.2021	−0.0096	−0.2690	0.1745	0.2450	−0.2280	0.0945
	6-31G*	−0.3464	−0.3669	0.0327	0.2213	−0.0205	0.3109	−0.2069	−0.2809	0.2549	0.1040
3	3-21G	−0.2791	−0.2149	0.1840	0.2447	0.0344	0.2301	−0.1903	−0.1984	0.2464	−0.0163
	6-31G*	0.3247	0.2523	−0.2180	−0.2857	0.0390	0.2591	−0.2236	−0.2306	0.2793	−0.0202

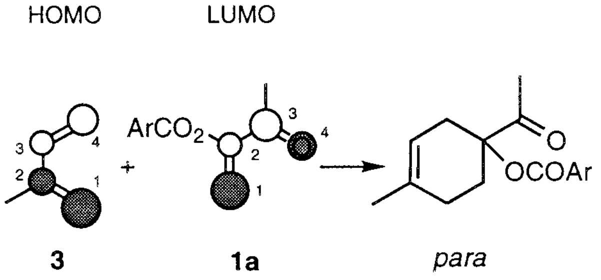
[a] These are the values of the $2p_z$ coefficients; the relative $3p_z$ contributions and their ΔC_i are analogous. [b] Coefficients of 2NHOMOs of olefin **1a**, since the HOMOs and NHOMOs do not have p_z contribution. [c] Coefficients of NLUMOs of olefin **1a**, since the LUMOs do not have p_z contribution. [d] The FMOs of the nonplanar *s-trans* conformation for **1a** and *s-cis* for MVK and **3**. [e] Carbon 1−carbon 2 for the olefins; carbon 1−carbon 4 for the diene.

TABLE 8: Energy Gaps (eV) of Frontier Molecular Orbitals[a] **for Dienophile 1a**[b] **and Diene 3**

method	HOMO−LUMO	LUMO−HOMO	diff
3-21G	10.9524	14.5911	3.6387
6-31G*	11.0781	14.5460	3.4679

[a] HOMO-diene/LUMO-dienophile and LUMO diene/HOMO-dienophile. The gaps for dienophile **1a** were calculated with the 2NHOMO and NLUMO, since its HOMO and LUMO do not have a p_z contribution. [b] Of the nonplanar *s-trans* conformation.

SCHEME 2: Ab Initio RHF/6-31G* Frontier Molecular Orbital Interaction for the Diels−Alder Reaction between Olefin 1A and Diene 3



hindrance[4c,5,29,32] could also be considered as controlling both reactivity and selectivity. These factors may be particularly important in 1,3-dipolar cycloadditions of **1a**, in which the FMO model does not predict the experimental regiochemistry.[5] In these cases, a stepwise reaction or a diradical transition state could be suggested.[1b,33]

The high regioselectivity shown by these molecules in Diels−Alder additions has been previously explained by the FMO treatment with ab initio STO-3G calculations.[4a] The reliability of these calculations is now supported by their agreement with our improved calculations. The energetically favored interaction between dienophile **1a** with an electron-donor diene such as isoprene (**3**) is under NED, because the energy gap HOMO-diene/LUMO-dienophile is smaller than that of LUMO-diene/HOMO-dienophile by ca. 3.47 eV (6-31G*, Table 8). The relative magnitude of the MO coefficient of the olefin unsubstituted terminus, C-1, is increased at the expense of the coefficient of the substituted terminus, C-2, in both HOMO and LUMO (Table 7). Hence, the *para* regioisomer is expected to be the major product (Scheme 2), in accordance with the molecular orbital interaction LUMO-dienophile/HOMO-diene. This prediction agrees with the experimental results.[4]

3. Conclusions

The present spectroscopic, structural, and theoretical study of the captodative olefin **1a** reveals that the preferential conformation of the enone π system is the *s-trans*, in the crystal, solution, and gas phases. In addition, the IEs and EAs, as well as the calculated FMOs, predict a similar reactivity behavior for **1a** and MVK, suggesting a nonsignificant electronic effect from the electron-donor group. The steric effect created by the latter would be at the origin of the slight decrease in reactivity of olefins **1**, in Diels−Alder and 1,3-dipolar cycloadditions. The ab initio RHF/3-21G and 6-31G* calculations support the results of previously reported calculations at the lower STO-3G level, predicting the correct regioselectivity of this kind of captodative dienophiles in reactions with isoprene (**3**) and probably with other electron-donor monosubstituted dienes.

4. Experimental Section

Olefin **1a** was prepared as described;[6b] and the pale yellow crystals were recrystallized (hexane/AcOEt, 9:1), giving colorless crystals. These were mounted in glass fibers. Crystallographic measurements were performed on a Siemens P4 diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å; graphite monochromator) at room temperature. Two standard reflections were monitored periodically; they showed no change during data collection. Crystal data and data collection parameters are summarized in Table 1. Unit cell parameters were obtained from least-squares refinement of 26 reflections in the range $2 < 2\Theta < 20°$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all nonhydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates refined. Unit weights were used in the refinement. Structures were solved using SHELXTL[34] on a personal computer.

The UP spectra were obtained with a Perkin-Elmer PS18 photoelectron spectrometer with a He(I) source and connected to a Datalab DL400 signal analysis system. The bands, calibrated against rare-gas lines, were located using the position of their maxima, which were taken as corresponding to the vertical ionization energies. The accuracy of the IE values was estimated to be better than ±0.05 eV.

The ET spectroscopy apparatus is in the format devised by Sanche and Schulz[14] and has been previously described.[23] The ET spectra were obtained by operating the instrument in such a mode to obtain a signal related to the nearly total scattering cross section. The energy scales were calibrated using the ($1s^2$-$2s^2$) ^2S anion state of helium, and the estimated accuracy of the measured AE values is ±0.05 eV.

The ab initio SCF/RHF calculations were carried out with the 3-21G and 6-31G* basis sets using MacSpartan.[35] Geometries were optimized by using the AM1 semiempirical method,[36] and these were employed as starting point for optimization at the 3-21G and 6-31G* levels.

^1H NMR experiments were carried out on a Varian Gemini-300 (300 MHz) instrument with $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane as internal standard.

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