

- 97, 173 (1975).
 (4) G. C. Pappalardo and S. Gruttadauria, *Z. Phys. Chem. (Frankfurt am Main)*, **94**, 179 (1975).
 (5) G. C. Pappalardo, K. J. Irgolic, and R. A. Grigsby, *J. Organomet. Chem.*, **133**, 311 (1977).
 (6) E. Breitmaier, K.-H. Spohn, and S. Berger, *Angew. Chem., Int. Ed. Engl.*, **14**, 144 (1975).
 (7) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961.
 (8) J. R. Lyerla, Jr., and G. C. Levy, "Topics in ^{13}C NMR", Vol. I, Wiley-Interscience, New York, N.Y., 1974.
 (9) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **55**, 1985 (1971).
 (10) G. C. Levy, D. M. White, and F. A. L. Anet, *J. Magn. Reson.*, **6**, 453 (1972).
 (11) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Am. Chem. Soc.*, **95**, 1527 (1973), and references cited therein.
 (12) G. C. Levy, T. Holak, and A. Steigel, *J. Am. Chem. Soc.*, **98**, 495 (1976).
 (13) For a review see also ref 6 and 8.
 (14) A. Forchioni, V. Galasso, K. J. Irgolic, and G. C. Pappalardo, *J. Organomet. Chem.*, **135**, 327 (1977).
 (15) D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *J. Chem. Phys.*, **50**, 719 (1969).
 (16) R. E. Marsh, *Acta Crystallogr.*, **5**, 458 (1952).
 (17) J. D. Lee and M. W. R. Bryant, *Acta Crystallogr., Sect. B*, **25**, 2094 (1969).
 (18) G. Llabres, O. Dideberg, and L. Dupont, *Acta Crystallogr., Sect. B*, **28**, 2438 (1972).
 (19) An analogous hypothesis of inverse proportionality between these parameters was recently adopted in ^{13}C T_1 studies of peptides; see R. L. Somorjai and R. Deslauriers, *J. Am. Chem. Soc.*, **98**, 6460 (1976).
 (20) D. Wallach, *J. Chem. Phys.*, **47**, 5258 (1967).
 (21) M. J. Aroney, S. W. Fillipcuck, and D. V. Radford, *J. Chem. Soc., Perkin Trans. 2*, 695 (1975).

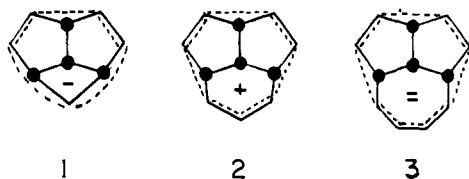
Photoelectron Spectra and Orbital Interactions in Methylenenortriquinacenes

L. N. Domelsmith,¹ K. N. Houk,^{*1,2} C. R. Degenhardt,^{3,4} and L. A. Paquette³

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received April 21, 1977

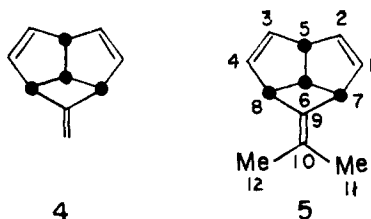
Abstract: Analysis of the photoelectron spectra of nortriquinacene (**6**), 2-methylenenortriquinacene (**4**), 2-isopropylidenenortriquinacene (**5**), and their tetrahydro derivatives has confirmed that the exocyclic double bond does not interact with the endocyclic π bonds. Additionally, it has been possible to demonstrate that the order of the latter orbitals is normal (A over S), in agreement with ab initio STO-3G calculations, but not with MINDO/2 and -3 calculations. These findings agree well with existing chemical and spectroscopic evidence as to the lack of homoaromaticity in these compounds and analogous trishomocyclopentadienides.

Recently, Paquette and co-workers successfully synthesized several precursors to the trishomocyclopentadienide anion **1**, but found no evidence for homoaromaticity in these



systems.⁵ Similarly, attempts to generate the trishomotropylum ion **2**⁶ and trishomocyclooctatetraenide dianion **3**⁷ showed homoaromatic stabilization to be lacking in these species. Calculations are also in agreement with the absence of significant conjugation in such systems. For example, **1** is predicted by MINDO/3 to have a pyramidal rather than trigonal anionic carbon.⁵ Furthermore, exomethylene derivatives of nortriquinacene show no chemical or ^{13}C spectroscopic evidence for homoconjugative interaction.⁵

We have now used a sensitive probe of orbital interactions, photoelectron (PE) spectroscopy, as well as ab initio molecular orbital (MO) calculations, to investigate the orbital interactions present, or absent, in the methylenenortriquinacenes **4**



and **5**. In particular, the main question to be answered in this study was whether the apparent lack of interaction in these systems is due only to poor overlap of component π orbitals with each other, or whether some combination of conjugative (through-space) and hyperconjugative (through-bond) interactions present in the particular carbon skeletons studied cancels stabilizing interactions which might otherwise take place.

Photoelectron Investigations of π Ionizations. Photoelectron spectroscopy is a sensitive probe of interaction between π systems. For example, three ethylenic π orbitals unite in the benzene molecule to form the familiar degenerate HOMOs and a lower energy π orbital; the PE spectrum shows that there is a 3-eV difference between the energies required to remove electrons from these two types of orbitals. Thus, ionization potentials (IPs) of 9.24 and 12.3 eV are observed in the benzene molecule,⁸ and these can be equated to the negatives of the orbital energies of the molecule, using Koopmans' theorem.⁹ Using a linear combination of bonding orbitals (LCBO) model in which three isolated π orbitals interact to form the orbitals of benzene, and neglecting overlap, the 3-eV split translates into a resonance integral of 1 eV resulting from π interactions of ethylene units separated by 1.397 Å.

In 1,4,7-cyclononatriene (trishomobenzene), a 0.9-eV split between the degenerate highest occupied molecular orbitals (HOMOs) and the lowest π orbital¹⁰ indicates a resonance integral of 0.3 eV, resulting from the mixed σ and π interactions of ethylenic units separated by 2.46 Å.¹¹ In triquinacene (a trishomobenzene), a split of only 0.35–0.4 eV¹² leads to a lower limit of 0.1 eV for the resonance integral between the π orbitals of ethylene units separated by 2.533 Å.¹³ This is a lower limit, since hyperconjugative interactions are believed to destabilize the lowest π orbital in this molecule,¹² making

Table I. Ionization Potentials of Nortriquinacenes and Analogues^a

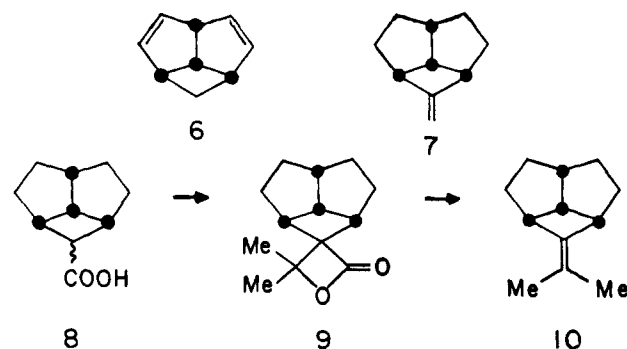
Compd	First IP	Second IP	Third IP	σ onset	Ref
11	9.00	9.35		10.70	26
12	9.0	9.5		10.4	12
6	8.76 (A) 8.83 (V)	9.26 (V)		10.4	This work
7	8.87 (A) 9.13 (V)			10.0	This work
4	8.80 (V)	9.23 (V)	9.47 (A) 9.63 (V)	10.7	This work
10	8.19 (A) 8.35 (V)			9.7	This work
5	8.15 (A) 8.31 (V)	8.71 (V)	9.28 (V)	10.5	This work

^a A = adiabatic IP; V = vertical IP.

the split smaller than it would be if only through-space conjugative interactions were operative.

The extent of interaction measured by PE spectroscopy does not, however, directly reflect the extent of stabilization conferred upon a molecule by interaction. In fact, the interaction of filled orbitals leads to destabilization (closed-shell repulsion),¹⁴ which increases as the overlap between filled orbitals increases. The extent of stabilization attending interaction of several π orbitals is related to the magnitude of mixing of filled orbitals on one fragment with vacant orbitals on the other. While photoelectron spectroscopy could, in principle, detect this mixing by providing a measure of the difference between an actual IP and one that the system would have without filled-vacant interactions, the latter can only be estimated or calculated. The difficulty in choosing appropriate models is reflected in the following example: benzene and fulvene are isomers, the π systems of which can be formally derived from those of butadiene and ethylene. It is well known experimentally that benzene is highly stabilized (aromatic), but that fulvene is a normal, if polarized, polyolefin. Nevertheless, the sums of the π orbital energies as measured by PE spectroscopy for benzene ($9.24 + 9.24 + 12.3 = 30.8$ eV)⁸ and for fulvene ($8.55 + 9.54 + 12.8 = 30.9$ eV)¹⁵ are nearly identical and quite similar to the sum of the π orbital energies of butadiene and ethylene ($9.07 + 11.47 + 10.51 = 31.0$ eV).¹⁵ In spite of this limitation of PE spectroscopy in detecting aromaticity, the tool is a powerful one for determining the interaction of occupied orbitals from which inferences about stabilization can be made.

Synthetic Considerations. Hydrocarbons 4–7 were available from the earlier study.⁵ The isopropylidene derivative 10 was elaborated by treatment of carboxylic acid 8⁵ with 2 equiv of



lithium diethylamide and acetone, followed by benzenesulfonyl chloride in pyridine.¹⁶ When heated to 120 °C, the β -lactone so produced (9) underwent smooth decarboxylation with specific introduction of the desired double bond.

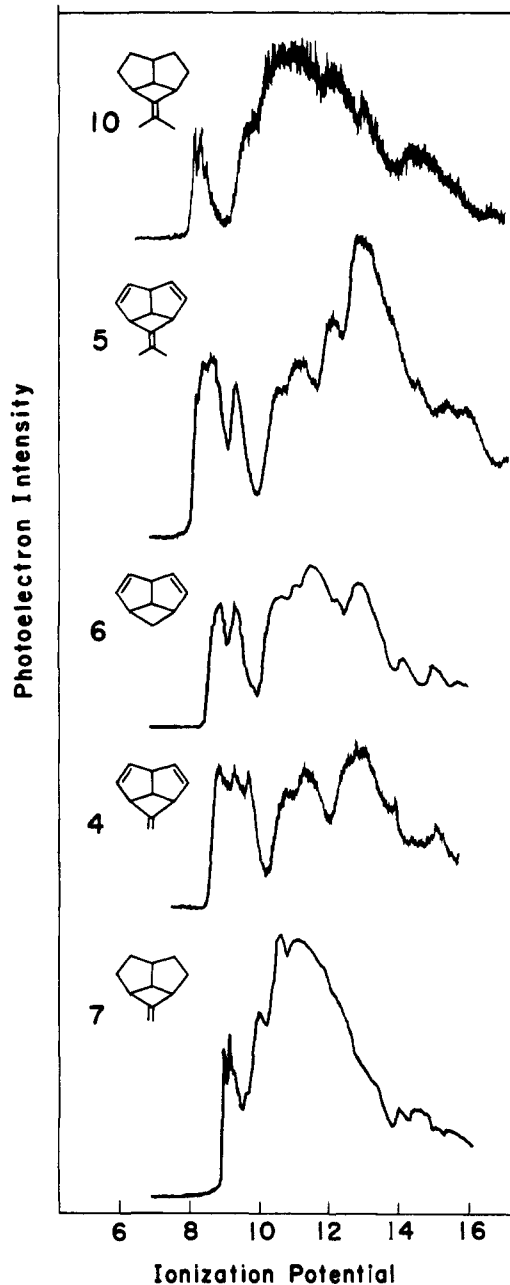
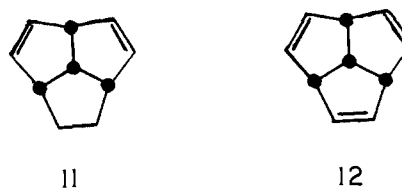


Figure 1. Photoelectron spectra of 10, 5, 6, 4, and 7.

Photoelectron Spectra of the Nortriquinacenes and Model Alkenes. The photoelectron spectra were measured with a Perkin-Elmer PS-18 photoelectron spectrometer using an He(I) source and Xe and Ar as internal calibrants. The spectra of the molecules studied here are shown in Figure 1 and the values of vertical ionization potentials are given in Table I, along with those of the related compounds dihydrotriquinacene (11) and triquinacene (12) studied earlier by others.



In both of the monoalkenes 7 and 10, the lowest IP shows vibrational structure characteristic of ionization from an alkene π orbital. The vibrational energy spacing of 0.16 eV is the same

as that observed in a variety of monoalkenes,^{17,18} as are the similar intensities of 0-0 and 0-1 vibrational bands, and the rapid decrease in the intensity of the 0-2 and 0-3 bands.¹⁸ The vibration excited is the CC stretching in the radical cation state.¹⁷

Methylenetetrahydronortriquinacene (**7**) has a vertical (0-1) IP of 9.13 eV, somewhat lower than those of isobutene (0-0 at 9.23 eV, 0-1 at 9.41 eV)¹⁹ and methylenecyclobutane (0-0 at 9.18 eV, 0-1 at 9.35 eV).¹⁹ Isopropylidenetetrahydronortriquinacene (**10**) has a vertical (0-1) band at 8.35 eV, which corresponds closely to that of 2,3-dimethyl-2-butene (0-0 at 8.31 eV, 0-1 at 8.47 eV).²⁰ In both of the monoalkenes, the tetrahydronortriquinacene framework causes a small (0.12-0.28 eV) destabilization of the π orbital as compared to the dimethyl analogues.

The photoelectron spectrum of nortriquinacene (**6**, Figure 1) shows two resolved bands. The first has an adiabatic transition at 8.76 eV, which is nearly the same in intensity as the second prominent maximum at 8.83 eV. The second band has some vibrational structure with a definite maximum, the vertical IP, at 9.26 eV. The 0.5-eV difference in the first and second IPs as well as the shapes of the two bands are uncannily similar to the corresponding features in the photoelectron spectra of 1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene.²¹ These compounds have separations of 0.34, ~0.4, and 0.41 eV, respectively, between their first and second IPs. Bünzli and co-workers concluded on the basis of calculations, as well as the small increase in IP separations along this series, that the through-space bonding combination (S) of orbitals was lower in energy than the through-space antibonding (A) combination.²¹ If through-bond coupling were more important than through-space coupling, then the S over A order would hold, but a decrease in split along the series would have been expected as through-bond coupling decreased.

In nortriquinacene (**6**), the first band has a vibrational spacing of 0.15 eV, and the second band has spacings of 0.08 and 0.17 eV, similar to those of 0.15 eV in the first bands, and 0.17-0.20 eV in the second bands of Bünzli et al.'s acyclic compounds.²¹ Assuming their conclusion to be correct, the similarity in vibrational spacing suggests that the through-space antibonding combination (A) of π orbitals in **6** is higher in energy than the bonding (S) combination.

The IP values of **6** unfortunately do not provide clear-cut evidence on the order of orbital energies. The average of the first two (9.01 eV) is quite similar to the IP expected for dihydronortriquinacene (8.9 eV). The last estimate was made in the following way: the conversion of 1-butene to 1-pentene (β -methylation) causes a 0.10-eV decrease in IP, while conversion of 1-butene to 3-methyl-1-butene (α -methylation) causes a 0.09-eV decrease in IP.²² Cyclopentene has a vertical IP of 9.18 eV²³ (or 9.20 eV),²⁴ and two α and one β substituents are expected to decrease this IP by about $2(0.10) + 0.09 \approx 0.3$ eV. Thus, dihydronortriquinacene should have an IP of approximately $9.2 - 0.3 = 8.9$ eV.

If there were an unusually large hyperconjugative (through-bond) destabilization of the S orbital in **6**, the average IP might be expected to be lower than that of the monoalkene, whereas experimentally, the average IP is higher. Unfortunately, this argument is not supported by experimental data on molecules with the A over S, or the S over A, order of orbital energies. Thus, norbornadiene, which has the S orbital below the A, has an average π IP of 9.12 eV, 0.15 eV higher than that of norbornene (8.97 eV),^{24,25} while 1,4-cyclohexadiene, which has the A orbital below the S, has an average π IP of 9.30 eV, 0.18 eV higher than that of cyclohexene (9.12 eV).²⁵

The difference in energy between the π orbitals of **6** is consistent with the A over S order of orbitals. Thus, the 0.5-eV split is smaller than that in norbornadiene (0.9 eV),²⁴ consistent with the poorer overlap in **6**. The π orbitals in norbornadiene

are separated by 2.5 Å, while the separation of the nearest termini in **6** should be close to the 2.53-Å separation in triquinacene.¹³ The other termini of the nortriquinacene double bonds should be separated by about 3.78 Å.

Dihydrotriquinacene (**11**) has a somewhat smaller split (0.35 eV)²⁶ than that in **6**, and has been assigned the A over S order. The smaller split in this homologue may be due to somewhat poorer overlap than in **6**, where the deletion of a methylene group may bring the π orbitals into closer proximity. As shown below, there may be additional destabilization of the A orbital due to interaction with a Walsh cyclobutane orbital of A symmetry.

The most compelling evidence for the order of orbital energies comes from the observation of orbital energy changes which occur upon substitution of an exocyclic double bond on the four-membered ring. Such an orbital can interact through space with the S orbital of nortriquinacene, but not with the A. Similar symmetry-imposed selective interactions have been used to prove the order of orbital energies in norbornadiene.

As concerns **4**, three maxima are seen at 8.80, 9.23, and 9.63 eV. The first band has vibrational spacings of 0.06 and 0.16 eV, like that of the first band of **6**. The second band is relatively featureless. The third band has a maximum at 9.63 eV, but a barely discernible maximum at 9.47 eV is at the correct position and the proper relative intensity to be the 0-0 (adiabatic) transition of the third band. This interpretation implies a close correspondence between the third IP of the triene and the π IP of the monoene model. Accepting the correspondences gleaned here from vibrational structure implies that the first band of **4** arises from an orbital essentially identical with the antibonding combination of endocyclic π orbitals. The introduction of the exocyclic double bonds causes only a 0.04-eV stabilization of this orbital. The bonding combination of endocyclic double bonds is also affected to a small extent, increasing in energy by 0.02 eV, smaller than experimental error.

The exocyclic π orbital, which we interpret as having a 0-1 component at 9.63 eV in the triene, is stabilized by 0.50 eV as compared to the 0-1 band in the monoene model. This stabilization compares to the 0.4-eV stabilization of the π orbital of 1-pentene by introduction of a $\Delta^{4,5}$ double bond, as measured by the difference between the IP of 1-pentene (9.54 eV) and the average of the 1,4-pentadiene IPs (9.95 eV).²¹

There is a very small conjugative interaction, at best, between the exocyclic and endocyclic double bonds. The 0.5-eV stabilization of the exocyclic π orbital is due in part to inductive stabilization resulting from conversion of four sp^3 centers to four sp^2 centers, but there may be a small (~0.1 eV) stabilization resulting from mixing with the higher energy endocyclic S orbital. The changes in both endocyclic orbital energies are small, but the lowest IP is detectably stabilized with respect to the second. Both endocyclic orbitals of **6** should be stabilized inductively by introduction of the exocyclic double bond. For reference, the S orbital of norbornadiene is stabilized by 0.1 eV by introduction of an exocyclic double bond at C-7.²⁷ The small decrease in the second IP of **6** upon introduction of the exocyclic double bond is consistent with the assignment of the second IP as that arising from the S orbital, which is stabilized by inductive interaction and destabilized by conjugative interaction with the exocyclic double bond.

Isopropylidenenortriquinacene (**5**) has one richly complex band encompassing two ionizations, and a third, relatively sharp ionization band. The first band has a sharp peak at 8.15 eV, separated from the first distinct maximum at 8.31 eV by the 0.16-eV separation observed in the monoalkene model. The 8.31-eV maximum thus appears to be the 0-1 band of the exocyclic π orbital, essentially unchanged from its position in **10** (8.35 eV). The second maximum at 8.71 eV is slightly lower than the first IP of **6** (8.83 eV), while the third is similar in

Table II. π Ionization Potentials (Negatives of Orbital Energies) Obtained from Calculations^a

Molecule	STO-3G	MINDO/2	MINDO/3
6	7.51 (A)	9.06 (S)	9.16 (S)
	7.78 (S)	9.33 (A)	9.18 (A)
4	7.49 (A)	9.01 (A)	9.01 (A)
	7.90 (S)	9.03 (S)	9.14 (S)
5	8.02 (X)	9.57 (X)	9.51 (X)
	7.08 (X)	8.74 (X)	8.70 (X)
	7.38 (A)	8.86 (A)	8.94 (A)
	7.82 (S)	9.01 (S)	9.24 (S)

^a A = orbital which is predominantly the antibonding combination of endocyclic double bonds; S = orbital which is predominantly the bonding combination of endocyclic double bonds; X = orbital which is predominantly the exocyclic double bond.

shape and at essentially the same position (9.28 eV) to the second band of **6** (9.26 eV).

In **5**, like **4**, there are very small interactions at best between the exocyclic and endocyclic double bonds.

When an isopropylidene group is substituted at C-7 of norbornadiene, the S orbital energy is unchanged. Conversion of **6** to **5** should cause only small inductive changes. The similarity in the exocyclic IP to that of the monoalkene model could arise from inductive stabilization counteracted exactly by conjugative destabilization. However, there is little evidence that the endocyclic orbital energies are changed. This is, however, consistent with the assignment of orbital energies (A over S) made for **6**. In **4**, some small interaction between the exocyclic and endocyclic S orbital occurs, whereas in **5** the exocyclic and endocyclic S orbitals are farther apart in energy, and the interaction is negligible. The opposite trend in interaction would be expected if S were above A in **6**.

The assignments made empirically are further supported by calculations described in the next section.

Calculations in the Nortriquinacenes. Calculations were carried out on **4–6** by ab initio calculations using the STO-3G basis set,²⁸ and by the semiempirical MINDO/2²⁹ and MINDO/3³⁰ techniques. Geometries for calculations by all these techniques were obtained in the following way: a trial geometry was obtained by using the x-ray crystallographic structure of **12**.¹³ Substitution of a methylene group for the ethylene group was made, and the resulting trial structure was optimized by MINDO/3. The distance between the closest double bond termini in **6** obtained in this way is 2.60 Å, somewhat larger than that in **12**. These geometries were then used to perform MINDO/2 and ab initio calculations, using the STO-3G basis set in the latter instance.

The results of these calculations are given in Table II. The STO-3G calculations agree completely with the empirical assignments given in the previous section. A least-squares correlation between the eight calculated π orbital energies and the corresponding IPs gives the correlation

$$\text{IP (eV)} = 1.28 (-\epsilon_{\text{STO-3G}}) - 0.72$$

with a correlation coefficient (r) of 0.978. For comparison, the correlation between STO-3G orbital energies and the π IPs of ten simple acyclic alkenes (ethylene and all methylated derivatives through tetramethylethylene, and monosubstituted alkenes through *tert*-butylethylene) is³¹

$$\text{IP (eV)} = 1.39 (-\epsilon_{\text{STO-3G}}) - 1.79$$

which has an r of 0.996. The MINDO/2 and MINDO/3 calculations give quite different results from the STO-3G. For **6**, both MINDO/2 and MINDO/3 place the S orbital above the A orbital in energy, although, in the case of MINDO/3, the energy gap is very small (0.02 eV). For **4** and **5**, MINDO/2

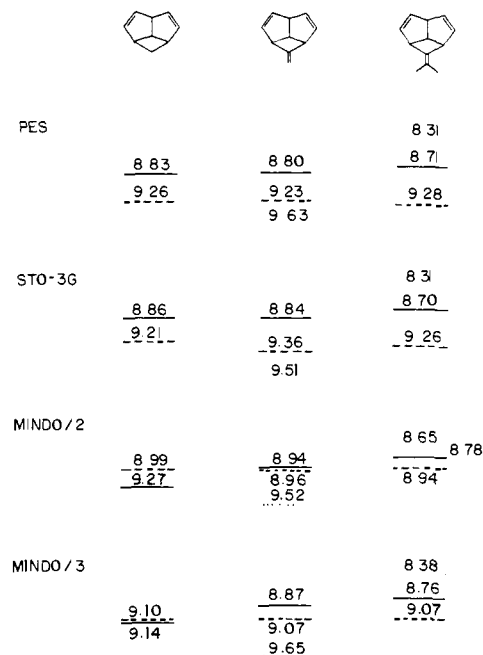


Figure 2. Experimental and calculated IPs of nortriquinacene and the alkylidene nortriquinacenes (—, A orbitals; ---, S orbitals; ···, exo π orbitals).

and MINDO/3 give the same orbital orderings as STO-3G. Least-squares correlations between the calculated π orbital energies and the corresponding IPs give the following correlations: for MINDO/2, with empirical assignments, $\text{IP} = 1.05 (-\epsilon_{\text{MINDO/2}}) - 0.49$ ($r = 0.67$), or, assuming that MINDO/2 assignments are correct, $\text{IP} = 1.33 (-\epsilon_{\text{MINDO/2}}) - 3.04$ ($r = 0.85$). For MINDO/3, with empirical assignments of IPs, $\text{IP} = 1.57 (-\epsilon_{\text{MINDO/3}}) - 5.25$ ($r = 0.89$), or without assignments of IPs $\text{IP} = 1.59 (-\epsilon_{\text{MINDO/3}}) - 5.49$ ($r = 0.91$). The different treatment of various types of interactions by the different calculational techniques is best seen in Figure 2, which compares the PE results and empirical assignments with those from the various types of calculations, corrected to give IPs according to the correlation equations given above.

Qualitative trends in photoelectron IPs are reliably reproduced by STO-3G, but not by MINDO/2 and MINDO/3, both of which predict a strong destabilization of the A orbital across the series, in contrast to PE IPs. Consistent with the PE results, MINDO predicts that the S diene orbital will remain approximately at the same energy. The tendency of MINDO/2 and MINDO/3 to overestimate through-bond interactions in comparison to through-space interactions results in an S over A orbital order in **6**. Gordon and co-workers have found that in MINDO resonance integrals fall off too rapidly with distance which leads to an underestimation of through-space effects.³² Both MINDO/2 and MINDO/3 are plagued by high-lying σ orbitals which leads to further exaggeration of σ/π mixing (through-bond interactions) and renders MINDO unreliable for small ring compounds.³³ In their analysis of through-bond and through-space effects in MINDO/2, SPINDO, and CNDO/2, Heilbronner and Schmelzer emphasized that correct orbital orderings for close-lying molecular orbitals by semiempirical methods is probably a fortuitous result of sums and differences of comparatively large simultaneous through-space and through-bond interactions.³³

Because the ab initio results seem to correspond more closely to the experimental results than the other types of calculations, we turn to an analysis of the STO-3G eigenvectors in order to see what the calculations say about the extent and types of interactions present in these molecules.

Table III. Summary of STO-3G Eigenvectors^a

Orbital symmetry ^b	6		4			5		
	A	S	A	S	S	S	A	S
Orbital energy, eV	-7.51	-7.78	-7.49	-7.90	-8.02	-7.08	-7.38	-7.82
Diene: 1(π)	0.43	0.40	0.42	0.39	0.28	-0.16	0.42	0.41
2(π)	0.45	0.43	0.44	0.42	0.13	-0.02	0.44	0.43
σ framework 5(CH π)		-0.29		-0.28				-0.29
6(CH π)		0.21		0.16				-0.20
7(CH π)		-0.12		-0.09				-0.14
9(CH π)		0.24						
Walsh cyclobutane: 6(CH ρ)	0.06		0.07				0.06	
7(CH ρ)	-0.18		-0.20				-0.21	
9(C ρ)	0.22		0.24				0.24	
Exo alkene: 9(π)				-0.27	0.55	0.60		0.22
10(π)				-0.24	0.60	0.50		0.03
Methyl: 11(CH ₂ π)							-0.20	-0.04

^a The numbers given are the square root of the sum of the squares of the coefficients of atomic orbitals at a given center. The signs indicate whether the orbitals on adjacent centers are bonding or antibonding. In all cases there is considerable delocalization in the molecular orbitals so that only coefficients for the major contributing centers are noted. ^b With respect to the plane of symmetry containing C-5, C-6, C-9, and C-10.

The STO-3G eigenvectors are summarized in Table III. The densities at various atoms or groups in various orbitals are shown. For **6**, the two high-lying occupied orbitals are the antibonding (A, HOMO) and bonding (S, SHOMO) combinations of the two homoconjugated π orbitals. This is the expected orbital order if interactions are predominantly through space. The A orbital is further destabilized by through-bond interactions with a lower energy Walsh cyclobutane A orbital. The extent of this interaction increases slightly across the series, pushing the A orbital up in energy. This increasing interaction results from increasing hyperconjugative interactions between the Walsh cyclobutane A orbital and the methylene and isopropylidene groups. Symmetry restrictions preclude interaction between the A diene orbital and the exocyclic double bond.

The behavior of the S endocyclic diene orbital is more complex: it is destabilized by hyperconjugative interactions with the nortriquinacene σ framework (particularly the methine CH orbitals), and is stabilized in **4** but destabilized in **5** by the exocyclic double bond. In the case of **4**, there is considerable mixing of the S diene orbital and the lower energy exocyclic π orbital; however, the presence of the methylene group perturbs the σ framework, resulting in decreased hyperconjugative interactions with the S diene orbital, as indicated by the smaller coefficients at the non- π carbons in the S orbital. The net effect of these interactions is a lowering of the S diene orbital energy in **4** relative to **6**. In **5**, the exocyclic double bond is strongly destabilized by hyperconjugative interactions with its methyl substituents so that it is pushed above both the S and A diene orbitals. The large S diene-exocyclic π orbital energy gap results in decreased through-space interaction, as indicated by the magnitudes of the coefficients. The S diene orbital of **5** is similar in energy and composition to that of **6** itself. The calculations indicate that the isopropylidene group perturbs the hyperconjugating σ framework to a much smaller extent than does the simpler methylene moiety.

Finally, we note that the very small interactions between the endocyclic and exocyclic double bonds in the alkylidenenortriquinacenes are fully compatible with the small polarization of the exocyclic double bond found in the ¹³C NMR spectra of these compounds. Dramatic polarization is observed in the exocyclic double bond in methylenenorbornadiene (the difference in ¹³C chemical shifts, $\Delta\delta^{13}\text{C}$, is 99 ppm as compared to a $\Delta\delta^{13}\text{C}$ of 61 in methylenenorbornane).²⁷ This polarization will occur by mixing of the π and π^* orbitals of the exocyclic double bond induced by overlap with the norbornadiene en-

docyclic orbitals. The PE spectrum indicates a 0.2–0.5-eV interaction between the exocyclic and endocyclic double bonds. In **4**, $\Delta\delta^{13}\text{C}$ is only 42 ppm, actually less than that in **7**.⁵ This is compatible with the very small (0.0–0.1 eV) interaction, and the dominant importance of inductive effects, or, more rigorously, the change in hyperconjugative abilities of the σ bonding orbitals as double bonds are introduced into the σ framework.

Experimental Section

Isopropylidenetetrahydronortriquinacene (10). Carboxylic acid **8** was prepared by catalytic hydrogenation of nortriquinacene-carboxylic acid. A solution of **8** (200 mg, 1.20 mmol) in 2 mL of dry tetrahydrofuran was added to one containing lithium diisopropylamide [prepared from 268 mg (2.65 mmol) of the amine and 1.27 mL of 2.08 M *n*-butyllithium in hexane (2.65 mmol)] in 3 mL of the same solvent. The mixture was allowed to warm to room temperature and then heated at 50 °C for 2 h. After cooling to -78 °C, acetone (70 mg, 1.20 mmol) was introduced via syringe and the mixture was kept at -23 °C for 2 h and at room temperature for 30 min before being poured onto ice (40 g). The mixture was extracted four times with ether; the aqueous phase was acidified with 3 N hydrochloric acid and reextracted with ether (4 × 25 mL). The latter organic layers were combined, dried, and evaporated to give 260 mg (96.3%) of hydroxy acid as a viscous yellowish oil which was used without further purification: ν_{max} (neat) 3020, 2900, and 1690 cm^{-1} ; $\delta_{\text{Me}_4\text{Si}}$ (CDCl₃) (60 MHz) 8.69 (br s, 2), 2.97–2.38 (m, 3), 2.06–1.40 (m, 9), and 1.30 (s, 6).

A cold (-5 °C) solution of the hydroxy acid (250 mg, 1.11 mmol) in dry pyridine (10 mL) was treated with benzenesulfonyl chloride (787 mg, 4.46 mmol) and stored at 0 °C for 23 h. The mixture was poured onto ice (40 g) and extracted with ether (5 × 25 mL). The combined organic layers were washed with saturated sodium bicarbonate solution, dried, and concentrated. Residual pyridine was removed at 0.5 mm. There was obtained 180 mg (78.3%) of **9**: ν_{max} (neat) 2940, 2870, and 1810 cm^{-1} ; m/e 206.1310 (calcd for C₁₃H₁₈O₂, 206.1307).

The unpurified β -lactone (150 mg, 0.727 mmol) was heated to 120 °C in a 25-mL round-bottomed flask fitted with a short-path condenser and maintained at this temperature for 10 min. NMR analysis indicated approximately 80% reaction. The material was vacuum transferred and subjected to preparative VPC purification (6 ft × 0.25 in. 12% Carbowax 20M, 110 °C). The hydrocarbon was isolated as a clear colorless liquid: $\delta_{\text{Me}_4\text{Si}}$ (CDCl₃) (90 MHz) 3.13–2.65 (m, 3), 2.58–2.33 (br s, 1), 1.82–1.55 (m, 8), and 1.55–1.52 (s with fine splitting, 6); m/e 162.1405 (calcd for C₁₂H₁₈, 162.1408).

Acknowledgments. Financial support of this research by the National Institutes of Health (GM-21311) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We wish to thank Professor Roald Hoffmann for stimulating discussions.

References and Notes

- (1) Louisiana State University.
- (2) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.
- (3) The Ohio State University.
- (4) Public Health Service Postdoctoral Fellow, 1977.
- (5) L. A. Paquette, H. C. Berk, C. R. Degenhardt, and G. D. Ewing, submitted for publication.
- (6) L. A. Paquette, P. B. Lavrik, and R. H. Summerville, submitted for publication.
- (7) L. A. Paquette, M. J. Kukla, S. V. Ley, and S. G. Traynor, submitted for publication.
- (8) L. Åsbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970); L. Åsbrink, O. Edqvist, E. Lindholm, and L. E. Selin, *ibid.*, **5**, 192 (1970).
- (9) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
- (10) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).
- (11) W. R. Roth, W. B. Bang, P. Göbel, R. L. Saas, R. B. Turner, and A. P. Yu, *J. Am. Chem. Soc.*, **86**, 3178 (1964).
- (12) J. C. Bunzli, D. C. Frost, and L. Weiler, *Tetrahedron Lett.*, 1159 (1973).
- (13) E. D. Stevens, J. D. Kramer, and L. A. Paquette, *J. Org. Chem.*, **41**, 2266 (1976).
- (14) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).
- (15) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).
- (16) A. P. Krapcho and E. G. E. Jahngen, Jr., *J. Org. Chem.*, **39**, 1322 (1974).
- (17) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970; see also A. Katrib and J. W. Rabalais, *J. Phys. Chem.*, **77**, 2358 (1973).
- (18) P. D. Mollere, K. N. Houk, D. S. Bomse, and T. H. Morton, *J. Am. Chem. Soc.*, **98**, 4732 (1976), and references cited therein.
- (19) K. B. Wiberg, G. B. Ellison, J. J. Wendoloski, C. R. Brundle, and N. A. Kuebler, *J. Am. Chem. Soc.*, **98**, 7179 (1976). These values are about 0.1 eV higher than those cited by other authors for the same compounds.²⁰
- (20) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973); the adiabatic IP is reported here. The value of the vertical IP is assumed based on vibrational spacings in related tetrasubstituted alkenes.¹⁸
- (21) J. C. Bunzli, A. J. Burak, and D. C. Frost, *Tetrahedron*, **29**, 3735 (1973).
- (22) P. Masclet, D. Grosjean, G. Mouvier, and J. Dubois, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 225 (1973).
- (23) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
- (24) E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta*, **55**, 1490 (1972), and references cited therein.
- (25) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).
- (26) P. Bischof, D. Bosse, R. Gleiter, M. J. Kukla, A. de Meijere, and L. A. Paquette, *Chem. Ber.*, **108**, 1218 (1975).
- (27) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).
- (28) STO-3G calculations used Gaussian 70, QCPE No. 236, by W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, and the STO-3G basis set described by W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (29) MINDO/2 calculations used OPTMO, QCPE No. 217, by A. Komornicki and J. McIver. MINDO/2 is described by M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).
- (30) MINDO/3 calculations used MINDO/3, QCPE No. 279, by M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and R. K. Bischof. MINDO/3 is described in R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).
- (31) A. Battaglia, L. N. Domelsmith, R. W. Strozier, J. A. Hall, and K. N. Houk, unpublished results.
- (32) M. D. Gordon, T. Fukunaga, and H. E. Simmons, *J. Am. Chem. Soc.*, **98**, 8401 (1976).
- (33) E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58**, 936 (1975).

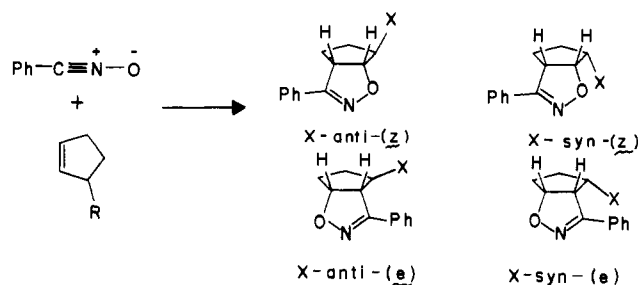
Photoelectron Spectra of 3-Substituted Cyclopentenes. Correlations between Ionization Potentials and Cycloaddition Regioselectivity

E. J. McAlduff,^{1a} Pierluigi Caramella,^{1b} and K. N. Houk*^{1c}

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received April 25, 1977

Abstract: The photoelectron spectra of 3-X-cyclopentenes, where X = methyl, ethyl, isopropyl, cyclohexyl, hydroxy, methoxy, acetoxy, dimethylamino, and phenyl, have been measured. The trend in ionization potentials is similar to that found for 3-X-propenes, but the changes are considerably smaller in the cyclopentenes. A simple model is developed relating the HOMO and LUMO coefficients of the substituted cyclopentene to the change in ionization potential caused by the substituent. A reasonable correlation is found between the regioselectivities of benzonitrile oxide cycloadditions to these cyclopentenes and a theoretical function of ionization potentials, $(9.18 - IP)(IP - 4.5)^{-1}$, which relates orbital coefficients and energies to ionization potentials.

Recently, Caramella and Cellerino reported a study of the products of cycloadditions of benzonitrile oxide to 3-substituted cyclopentenes (X-CP).² As shown in Scheme I, four



products can be obtained as a result of (1) cycloaddition to the same side of the cyclopentene ring as the substituent (syn ad-

dition) or to the opposite side (anti addition), and (2) cycloaddition with the oxygen of the nitrile oxide nearest the substituent (z addition) or furthest from the substituent (e addition).³ The products will be discussed here in terms of the nomenclature shown in Scheme I.

Caramella and Cellerino made the reasonable assumption that the ratio of z and e anti adducts would be a reflection of the electronic effect of the substituent, X, upon the double bond. That is, X does not interact through space with benzonitrile oxide when attacking from the anti side, so that the influence of the substituent on the ratio of isomers should result from alteration of the orbital energies and coefficients of the double bond.⁴ However, a plot of the ratio of isomers vs. Taft's polar substituent constant, σ^* (Figure 1), a commonly accepted measure of electron-donor or -acceptor potency of a substituent,⁵ shows some notable deviations from linearity, particularly for the phenyl, dimethylamino, and acetoxy substituents. A linear relationship might have been expected if the regioselectivity