# THE PHOTOELECTRON SPECTRUM OF TRIQUINACENE

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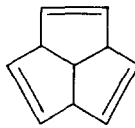
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The possibility of homo-aromaticity[2] existing in molecules with three properly disposed double bonds, such as cis,cis,cis-1,4,7-cyclononatriene (1)[3] and triquinacene (2)[4] has prompted a great deal of work with these systems. In the case of the cyclononatriene 1
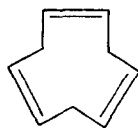

1   2

it was not possible by x-ray crystallography, nmr spectroscopy, or heats of hydrogenation to detect any interaction of the double bonds in 1.[3] Recently, however, Heilbronner and co-workers, using photoelectron spectroscopy, have been able to show that there is a significant interaction of the π bonds in 1.[5]

Several chemical and spectroscopic studies likewise failed to uncover any inter-action between the π bonds in triquinacene (2).[4] We have also turned to pes to determine if any interaction between the π levels in 2 can be detected. The He I pes[6] of 2, from 8.5 - 11.0 eV, is shown below. Because of the broadness of the bands in this spectrum it is diff-icult to obtain accurate ionization potentials and to make unambiguous assignments; however, we interpret the pes data as follows. The first vertical IP at 9.0 eV is assigned to ion-ization from the e(π) level. There is a noticeable broadening of this band which is consis-tent with a Jahn-Teller splitting of 0.2±0.1 eV, which is similar to the value found for the

e(π)

a$_1$(π)

Photoelectron Spectrum of Triquinacene ($\underset{\sim}{2}$).
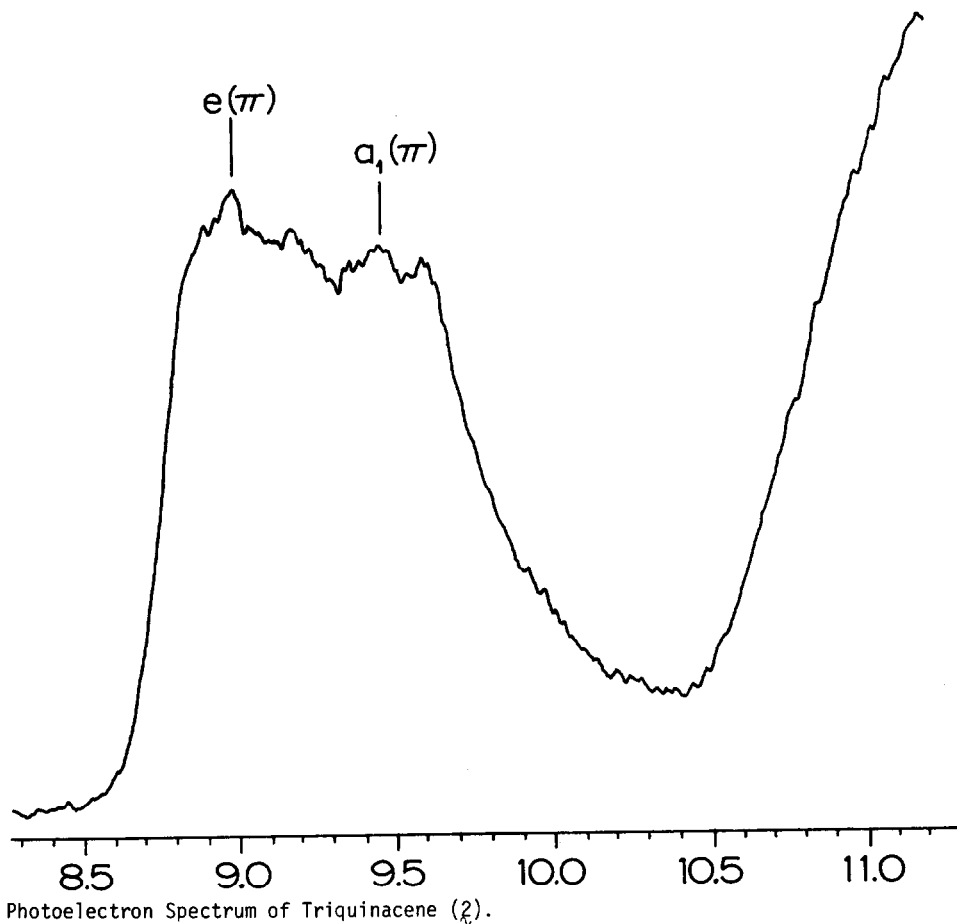
Jahn-Teller splitting of the e(π) ionization in $\underset{\sim}{1}$.[5] The second IP of $\underset{\sim}{2}$ at 9.5 eV is assigned to ionization from the a$_1$(π) level. A comparison of the π IP's of $\underset{\sim}{1}$ and $\underset{\sim}{2}$ is given in the table.

The Vertical IP's (eV) of $\underset{\sim}{1}$ and $\underset{\sim}{2}$.

Assignment	Cyclononatriene ($\underset{\sim}{1}$)[5]	Triquinacene ($\underset{\sim}{2}$)[7]
e(π)	8.77 8.9 - 9.0	9.0 9.2 - 9.3
a$_1$(π)	9.80	9.5
σ onset	10.9	10.4
δ(a$_1$ - e)	0.90 - 0.97	0.35 - 0.4

The pes of $\underset{\sim}{1}$ has been interpreted on the basis of a large through space interaction of the π levels and a small through bond interaction, leading to a large split in the $e(\pi)$ and $a_1(\pi)$ levels of $\underset{\sim}{1}$.[5] There is a much smaller split in the $e(\pi)$ and $a_1(\pi)$ levels of tri-quinacene ($\underset{\sim}{2}$). This could be due either to a smaller through space interaction of the π levels in $\underset{\sim}{2}$, relative to $\underset{\sim}{1}$, or to a larger through bond interaction involving the $a_1(\pi)$ and lower $a_1(\sigma)$ level(s). The through space interaction is related to the overlap of the orbitals involved and to their energy separation.[8] It is difficult to see how either of these effects could be significantly different in $\underset{\sim}{1}$ and $\underset{\sim}{2}$. Although the x-ray structure of triquinacene is not known, examination of various models indicates little difference, if any, in the arrange-ment of the double bonds in $\underset{\sim}{2}$ compared to the known geometry of $\underset{\sim}{1}$,[3d] which would imply a similar overlap of the π orbitals in both $\underset{\sim}{1}$ and $\underset{\sim}{2}$. This would lead to the expectation that the smaller splitting of the π levels in $\underset{\sim}{2}$ is due to a greater through bond interaction involving the a_1 levels. Indeed, CNDO/2 calculations for both $\underset{\sim}{1}$ and $\underset{\sim}{2}$ show this. Using the known geometry of $\underset{\sim}{1}$, the CNDO/2 calculations predict an $e(\pi),a_1(\pi)$ splitting of 1.29 eV, in reasonable agreement with the observed value of 0.90 - 0.97 eV.[5] Similar calculations for triquinacene ($\underset{\sim}{2}$), using a closely related geometry, predict a much smaller $e(\pi)$, $a_1(\pi)$ splitting, in the range of 0.1 eV. These calculations indicate that the $e(\pi)$ levels in both $\underset{\sim}{1}$ and $\underset{\sim}{2}$ are at about the same energy. However, the $a_1(\pi)$ level in $\underset{\sim}{2}$ is noticeably destab-ilized relative to the $a_1(\pi)$ level in $\underset{\sim}{1}$. This destabilization is due to an interaction of the $a_1(\pi)$ level with the $a_1(\sigma)$ level in $\underset{\sim}{2}$, which is comprised mainly of the three central C-C bonds and the central C-H bond, which supports the suggestion of a strong through bond interaction in triquinacene. Thus there is a much smaller overall interaction of the π levels in $\underset{\sim}{2}$ and it would not be surprising if this went undetected by the usual chemical methods.[4]

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