

# Electronic structure of the 6+6 dimer of tropone

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**ABSTRACT:** Photoelectron and electron transmission (ET) spectroscopy were used to determine the ionization potentials and vertical electron attachment energies, respectively, of the 6+6 dimer of tropone. These measurements are combined with electronic structure calculations to provide insight into the extent of the coupling between the two cycloheptadienone ring systems. The ground state anion is predicted to be slightly stable as a consequence of the interaction between the  $\pi^*$  orbitals of the C=O and butadiene groups. Copyright © 2006 John Wiley & Sons, Ltd.

**KEYWORDS:** tropone; photoelectron spectroscopy; electron transmission spectroscopy; orbital coupling

## INTRODUCTION

Dimers of aromatic compounds and cycloadducts with quinones are important intermediates in photochemical processes.<sup>1</sup> Their electronic structures are therefore of interest to synthetic as well as physical organic chemists. We present here studies on a simple system that incorporates several features of interest.

The 6+6 dimer of tropone (**1**) was first characterized in 1966.<sup>2</sup> Surprisingly little is known, however, about the electronic structure of this molecule. Of interest is the possibility that **1** might have an especially high-lying highest occupied molecular orbital (HOMO) or low-lying lowest unoccupied molecular orbital (LUMO) as a result of coupling<sup>3</sup> between the  $\pi$  or the  $\pi^*$  orbitals, respectively, of the two cycloheptadienone ring systems, perhaps mediated by through-space coupling with the carbonyl orbitals or through-bond coupling with the  $\sigma$  bonds joining the rings. To investigate this possibility, **1** was prepared and characterized by means of photoelectron and electron transmission (ET) spectroscopy. In addition, molecular orbital (MO) calculations were carried out to aid in the analysis of the spectra.

## PREPARATION AND X-RAY STRUCTURE

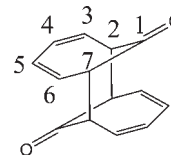
Tropone was prepared<sup>4</sup> and irradiated in a thin film reactor as reported by Reingold *et al.*<sup>5</sup> The 6+6 dimer

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was obtained in about 2–4% yield, and was identical to that reported by Mukai *et al.*<sup>2</sup>



**1**

The structure of **1** was determined by X-ray diffraction of a crystal sample. The crystal is found to belong to the monoclinic  $P2_1/c$  space group with two molecules in the unit cell, and accordingly the molecules are constrained to occupy inversion centers. The C=O bonds were of normal length (1.214(7) Å) as were the inter-ring bonds (1.557(8) Å). This result is of interest with respect to earlier discussions<sup>6–9</sup> concerning the lengthening of a C—C bond by through-bond interaction. Our results clearly demonstrate that bond lengthening by through-bond effects is not significant and confirm recent calculations.<sup>9</sup> The non-bonded distances between the carbonyl atoms and the diene ‘ribbons’ within and between units are summarized in Table 1.<sup>10</sup>

## PHOTOELECTRON AND ELECTRON TRANSMISSION SPECTRA

The He(I) photoelectron (PE) spectrum of **1** was obtained using a PS18 Perkin Elmer spectrometer. The spectrum, which is reproduced in Fig. 1, displays nine bands, listed

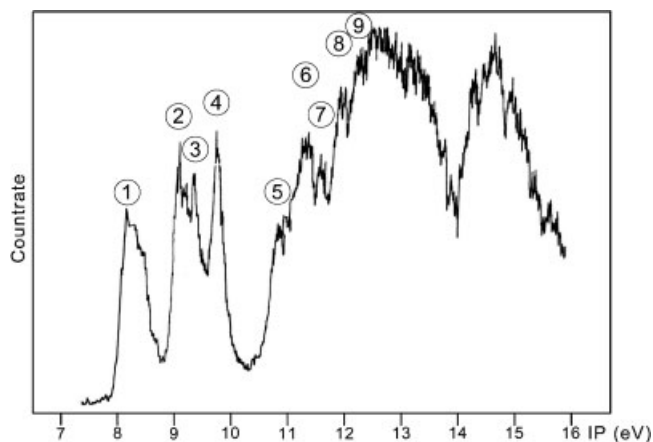
**Table 1.** Non-bonded distances (Å) for tropone dimer **1**

| Atoms | In same tropone unit | Between tropone units <sup>a</sup> |
|-------|----------------------|------------------------------------|
| C1-C3 | 2.479 (8)            | 3.191 (8)                          |
| C1-C4 | 2.976 (8)            | 3.563 (8)                          |
| C1-C5 | 2.968 (8)            | 3.546 (8)                          |
| C1-C6 | 2.477 (8)            | 3.160 (8)                          |
| O1-C3 | 3.284 (7)            | 3.880 (7)                          |
| O1-C4 | 3.798 (7)            | 4.079 (7)                          |
| O1-C5 | 3.795 (7)            | 4.061 (7)                          |
| O1-C6 | 3.293 (7)            | 3.845 (7)                          |

<sup>a</sup> Atoms are numbered to maintain a center of inversion, that is, C3 on the bottom tropone unit refers to the other side of the pseudo-mirror plane as C3 on top.

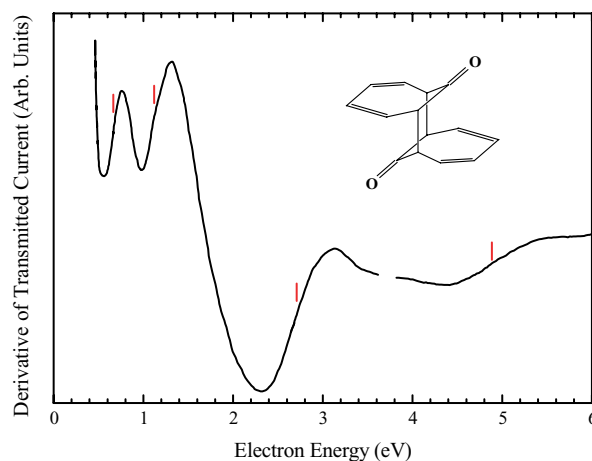
in Table 2, below 12.3 eV. Some of the bands, particularly the lowest energy band at 8.15 eV, are quite broad, and, *a priori*, it is not clear whether this is due to unresolved vibrational structure or to overlapping electronic states.

The temporary anion states of the tropone dimer were investigated using ET spectroscopy<sup>11</sup> to locate the sharp structure in the total electron scattering cross section. The application of this technique to hydrocarbon molecules has been reviewed elsewhere.<sup>12–14</sup> Energy scale cali-

**Figure 1.** Photoelectron spectrum of the 6+6 dimer of tropone. The labels correspond to the entries in Table 2**Table 2.** Comparison of the measured vertical ionization energies,  $I_v$ , and the calculated (6-31G(d) basis set) occupied orbital energies,  $-\epsilon$ , of the tropone dimer

| Band <sup>a</sup> | Assignment                     | Exp. $I_v$ (eV) | Theory $-\epsilon$ (eV) |
|-------------------|--------------------------------|-----------------|-------------------------|
| 1                 | (a <sub>u</sub> ) $\pi_2^+$    | 8.15            | 8.60                    |
| 2                 | (b <sub>g</sub> ) $\pi_2^-$    | 9.09            | 9.27                    |
| 3                 | (b <sub>g</sub> ) $n^-$        | 9.33            | 10.84                   |
| 4                 | (a <sub>u</sub> ) $n^+$        | 9.72            | 11.41                   |
| 5                 | (a <sub>g</sub> ) $\pi_1^+$    | 10.8            | 11.73                   |
| 6                 | (b <sub>u</sub> ) $\pi_1^-$    | 11.3            | 12.26                   |
| 8                 | (a <sub>g</sub> ) $\pi_{CO}^+$ | 11.9            | 12.69                   |
| 9                 | (a <sub>u</sub> ) $\pi_{CO}^-$ | 12.3            | 13.55                   |

<sup>a</sup> In assigning the spectrum, it has been assumed that the weak band 7 (at 11.6 eV) is due to a vibrationally excited level associated with the 11.3 eV band.

**Figure 2.** The derivative with respect to the energy of the transmitted electron beam current as a function of electron impact energy in the 6+6 dimer of tropone. The vertical lines locate the energies of the temporary anion states. The feature at 4.9 eV has been enlarged by a factor of 2.5

bration was carried out in an admixture of N<sub>2</sub> by reference to well-known structure in the 2 eV region.

The derivative with respect to energy of the electron current transmitted through vapor of the tropone dimer is shown in Fig. 2. Structures due to temporary anion formation are observed at 0.66, 1.12, 2.70, and 4.9 eV. The highest resonance is shown at enhanced gain (2.5×) to make it more apparent. Between 3 and 4 eV, there may also be evidence for a broad, weak resonance, the lower portion of which is obscured by the 2.7 eV structure. The uncertainties in the locations of the narrow features ascertained from the ET spectra are estimated to be ±0.05 eV.

## QUALITATIVE ANALYSIS

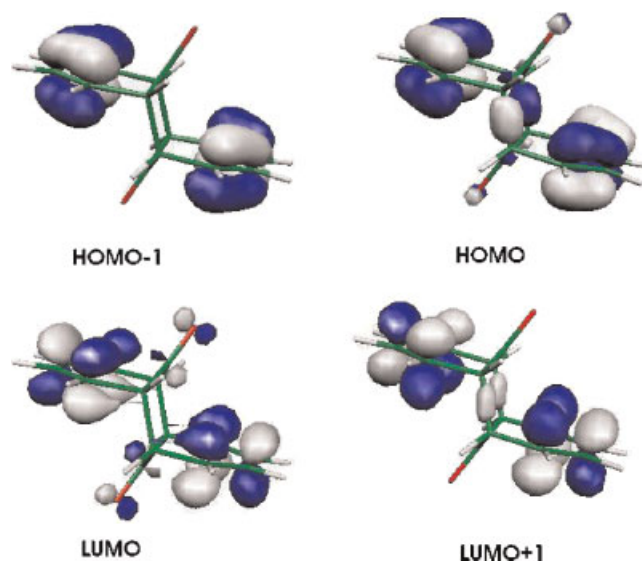
In analyzing the PE and ET spectra, we first make use of a reference compound approach. This is followed by a more detailed analysis using MO calculations. The two reference compounds are chosen to be 1,3-cycloheptadiene and cyclohexanone. The former has  $\pi$  ionization energies<sup>15</sup> of  $\pi_1 = 10.63$  eV and  $\pi_2 = 8.31$  eV; the latter<sup>16</sup> has an oxygen 2p lone-pair ionization energy of 9.14 eV and a broad peak near 11.4 eV which is thought to be due to ionization of the C=O  $\pi$  orbital.<sup>17</sup> Qualitatively, we expect that in **1** each of the bands will be split into a doublet as a result of the interactions between the ring systems. The splitting should be a bit less than 1 eV, as was observed in the related compound *anti*-tricyclo[6.4.0.0<sup>2,7</sup>]dodecatriene.<sup>18</sup> Therefore, one expects that the first two bands (at 8.15 and 9.09 eV) in the PE spectrum of **1** are assigned to the butadiene  $\pi_2^+$  and  $\pi_2^-$  linear combinations. The  $\pi$ -ionization energies are the net result of three effects: the opposing through-space (TS) and through-bond (TB) interactions and the stabilizing inductive effect of the carbonyl group. Bands 3 and 4 (at

9.33 and 9.72 eV) are assigned to ionization to the two combinations of the oxygen lone-pair orbitals, and bands 5 and 6 (at 10.80 and 11.30 eV) to ionization from the MOs derived from the butadiene  $\pi_1^+$  and  $\pi_1^-$  orbitals. At still higher energies the photoelectron spectrum of **1** has structure at 11.6, 11.9, and 12.3 eV. Based on comparison with the photoelectron spectrum of 1,4-cyclohexanedione,<sup>17</sup> we propose that the two bands at 11.9 and 12.3 eV are due to ionization from the C=O  $\pi$  MOs, with the feature at 11.6 eV likely due to an excited vibrational level of the 11.3 eV band. These proposed assignments, along with the results of the MO calculations discussed below, are listed in Table 2.

The  $\pi^*$  anion states of 1,3-cycloheptadiene are located<sup>19</sup> at 0.75 ( $\pi_3^*$ ) and 3.49 eV ( $\pi_4^*$ ), and the CO  $\pi^*$  anion state of cyclohexanone at 1.30 eV.<sup>20</sup> (These are vertical attachment energies (VAEs) and are the negatives of the vertical *electron affinities* with the standard sign definitions.) In a similar manner to the filled  $\pi$  energies, the  $\pi^*$  anion states of 1,3-cycloheptadiene are stabilized by the inductive effect of the carbonyl group. In **1**, the butadiene-like  $\pi_3^*$  and the CO  $\pi^*$  orbitals are expected to give rise to a total of four anion states lying below about 2 eV, but the ET spectrum displays only two distinct features. There are two possible interpretations of this result: (1) the interactions between the  $\pi^*$  orbitals on the two cycloheptadienone rings are negligible, with the result that each of the 0.66 and 1.12 eV features in the ET spectrum of **1** actually corresponds to two nearly degenerate anion states, or (2) the interactions are sufficiently large that one, or possibly two, of the anion states expected in this energy range are 'pushed' to such low energies that they cannot be observed in ETS. Formation of a stable anion state cannot occur with a free electron. Unstable anion states lying below approximately 0.3 eV may also be difficult to observe with ETS because of the sharply falling background owing to the wing of the electron beam energy distribution. Two additional anion states, derived from the butadiene  $\pi_4^*$  orbitals, are anticipated near 3.5 eV, based on the results in 1,3-cycloheptadiene.<sup>20</sup> Above this energy, anion states in which electron attachment is accompanied by promotion of an outer valence electron, that is, core-excited resonances, are likely, as well as states derived from empty  $\sigma^*$ (C–H) orbitals. The latter are generally too broad to be individually distinguished.

## ANALYSIS OF THE PE AND ET SPECTRA WITH THE AID OF MO CALCULATIONS

To quantify the analysis presented above, we have carried out *ab initio* electronic structure calculations on **1**, as well as on related model compounds. The calculations were carried out using GAMESS<sup>21</sup> and employed 6-31G(d) basis sets for geometry optimization of the neutral molecule and for the electron structure.



**Figure 3.** Molecular orbital plots of the two highest occupied molecular orbitals and two lowest normally unoccupied molecular orbitals

Table 2 summarizes the experimental IPs of **1** and the filled orbital energies obtained at the Koopmans' theorem (KT)<sup>22</sup> level. In the KT approximation, the IPs are associated with the negatives of the energies of the filled MOs. This approximation is a frozen-orbital model and thus neglects relaxation and correlation effects.

As expected, the two highest occupied MOs of **1** are derived from the  $\pi_2$  orbitals localized on the butadiene fragments. These are followed by the two CO lone-pair orbitals, and then by the two MOs derived from the  $\pi_1$  orbitals of the butadiene fragments. The seventh and eighth highest occupied MOs are associated with the CO  $\pi$  orbitals. Each of these pairs of orbitals is appreciably split (by 0.53–0.86 eV), indicating sizable interactions. Moreover, for each of the three pairs of  $\pi$  MOs, the '–' combination is predicted to be more stable than the '+' combination, as expected where TB coupling is more important than TS interaction. Orbital pictures of the HOMO and HOMO-1 filled orbitals are shown in the upper half of Fig. 3.

As shown in Table 3, the trends in the calculated virtual orbital energies (VOEs), associated with the anion states

**Table 3.** Comparison of the calculated KT VOEs, scaled VOEs, and measured VAEs of the tropone dimer in eV

| Assignment                     | KT VOEs | Scaled VOEs <sup>a</sup> | Expt. VAEs   |
|--------------------------------|---------|--------------------------|--------------|
| $\pi_3^*$ (b <sub>u</sub> )    | 2.4844  | 0.039                    | Not observed |
| $\pi_3^*$ (a <sub>g</sub> )    | 3.1701  | 0.474                    | Not observed |
| $\pi_{CO}^*$ (b <sub>u</sub> ) | 3.8314  | 0.893                    | 0.66         |
| $\pi_3^*$ (a <sub>u</sub> )    | 4.7266  | 1.461                    | 1.12         |
| $\pi_4^*$ (b <sub>g</sub> )    | 6.7838  | 2.765                    | 2.7          |
| $\pi_4^*$ (a <sub>u</sub> )    | 7.4178  | 3.167                    | 2.7          |
| Core-excited                   |         |                          | 4.9          |

<sup>a</sup> VAE = 0.634 VOE – 1.536.

of **1** by KT, are qualitatively in line with the expectations based on the reference molecule approach. Specifically, the two lowest energy  $\pi^*$  MOs are predicted to be associated with the butadiene  $\pi_3^*$  MOs, the middle two with the C=O  $\pi^*$  MOs and the highest two with the butadiene  $\pi_4^*$  MOs. The various pairs of  $\pi^*$  orbitals are split by 0.63–0.89 eV, indicating sizable interactions as found in the filled orbital manifold. Again, the  $\pi^*$  MOs derived from the butadiene  $\pi_3^*$  and  $\pi_4^*$  MOs have inverted (i.e., ‘–’ below ‘+’) orderings, indicating TB interactions. Pictures of the LUMO and LUMO+1 are given in the lower half of Fig. 3.

It is well known that KT VOs tend to be too high<sup>23–29</sup> relative to measured VAEs, with the error growing with increasing orbital energy. This is a consequence of the neglect of relaxation and correlation effects, as well as the missing interaction of the valence VO with the wave function of the continuum electron. However, plots of VOs as a function of measured resonance energies in unsaturated molecules show good correlations for the low-lying  $\pi^*$  resonances. By shifting and scaling the VOs semi-empirically, one may use such correlations to predict resonance energies in other compounds. Not surprisingly, the closer the structure of the molecules in the correlation are to those being studied, the better the predictive ability. The scaling parameters are, of course, a function of the basis sets employed. A variety of scaling expressions for different basis sets have been examined,<sup>28</sup> however the correlations have generally been determined ‘globally’ over a large set of rather different families of unsaturated molecules. For the present work, we have generated a scaling using compounds that are closer in structure to the moieties contained in the tropone dimer. Using the  $\pi^*$  anion states of butadiene,<sup>30</sup> formaldehyde,<sup>31</sup> 1,3-cycloheptadiene<sup>19</sup> and cyclohexanone<sup>20</sup> we find the following expression,

$$\text{VAE} = 0.634 \text{ VOE} - 1.536 \text{ (in eV)} \quad (1)$$

where VOE is the calculated energy of the unoccupied MO. The standard deviation of the fit is 0.2 eV.

The scaled KT results are compared with the energies of the features observed in the ET spectrum in Table 3. The anion states associated with the  $\pi^*$  carbonyl orbitals are predicted to lie at 0.89 and 1.46 eV, in reasonable agreement with the states observed at 0.66 and 1.12 eV, considering the scatter in the scaling expression. The predicted and experimental splittings agree to within 0.11 eV and support the assignment of these resonances to the  $\pi^*$  carbonyl groups.

The predicted energies of the resonances associated with the  $\pi_4^*$  butadiene MOs fall at 2.77 and 3.17 eV. The prominent feature observed at 2.70 eV is likely to be an unresolved composite of these two resonances. The leading term in a partial wave expansion of the wave function of the  ${}^2B_g$  resonance has angular momentum  $l = 2$ , suggesting a relatively long-lived temporary anion,

whereas the  ${}^2A_u$  companion has  $l = 1$  and thus may be shorter lived and broader.

The resonance deriving from the  $\pi_3^{+*}$  combination of the butadiene moieties is predicted at 0.47 eV. Unfortunately no evidence for resonance structure lying below the feature at 0.66 eV was observed. We note that if the predicted energies are shifted downward by 0.2–0.3 eV to agree with experiment at the  $\pi^*$  carbonyl resonances, then this resonance could lie at or below 0.25 eV, making it difficult to observe against the rising background. Although the ground state anion (resulting from occupation of the  $\pi_3^{+*}$  LUMO) is predicted to lie at 0.039 eV, this shift suggests that the ground state anion, in the geometry of the neutral, is *stable* with respect to the ground state of the neutral molecule.

## CONCLUSIONS

Photoelectron and ET spectra have been obtained for the 6 + 6 dimer of tropone. As the frontier orbitals pictured in Fig. 3 indicate, the HOMO displays a considerable TB coupling between the two ‘butadiene’ groups relayed through the saturated bridge. The LUMO, on the other hand, displays amplitude on the CO groups that indicates a stabilizing coupling between the carbonyl and butadiene localized  $\pi^*$  orbitals. Scaling of the KT VOs suggests that the ground state anion is slightly stable with respect to the neutral molecule.

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