

# A Photoelectron Spectroscopic Investigation of Tetra-*tert*-butyltetrahedrane and of Tetra-*tert*-butylcyclobutadiene

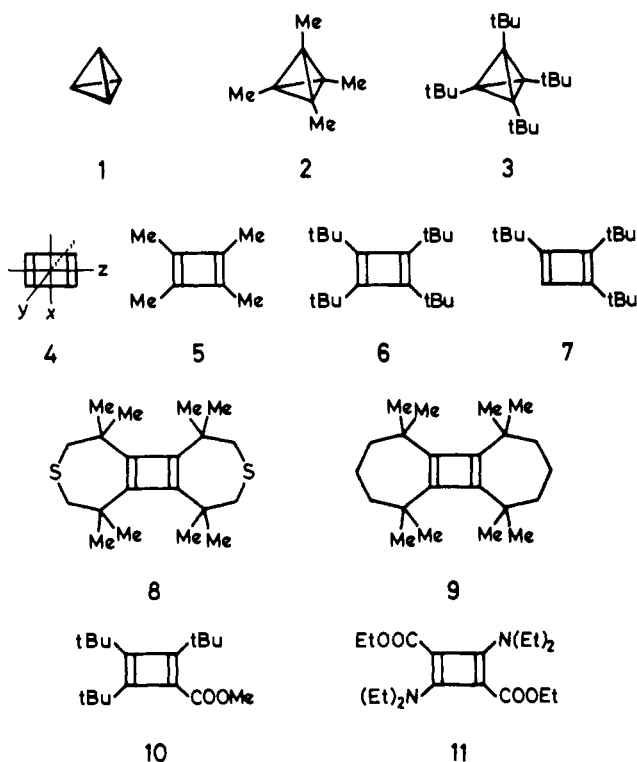
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**Abstract:** The He(I $\alpha$ ) photoelectron spectra of the title compounds tetra-*tert*-butyltetrahedrane (**3**) and tetra-*tert*-butylcyclobutadiene (**6**) and of the tricyclic hydrocarbon **9** (related to **6**) have been recorded and interpreted within Koopmans' approximation using ab initio and semiempirical model calculations. It is shown that removal of an electron from the highest occupied molecular orbital, of e symmetry, leads to a typical double-humped band with centroid  $I^c \approx 7.9$  eV, which is indicative of the expected Jahn-Teller distortion of the radical cation  $3^+$ . The rather good agreement between theory and experiment lends credibility to the conclusion derived from the theoretical calculations that in **1-3** the cross term between vicinal, localized CC  $\sigma$  orbitals (i.e., localized on two opposed edges of the tetrahedron) is practically zero, in contrast to the large interaction term between vicinal, localized CC  $\sigma$  orbitals in cubane. Comparison of our photoelectron spectroscopic results for **6** and **9** with those of other cyclobutadiene derivatives shows that the orbital sequence is  $\pi$  (=HOMO),  $\sigma$ ,  $\pi$ , in descending order, in agreement with previous theoretical predictions. The splits between the two  $\pi$  orbitals are  $\sim 3.9$  eV in **6** and  $\sim 3.5$  eV in **9**, i.e., close to an estimate extrapolated previously by Worley et al. from data on cyclobutadiene tricarbonyl complexes.

## Introduction

The recently reported synthesis of the tetra-*tert*-butyl derivative **3**<sup>3</sup> of tetrahedrane, **1** (=tricyclo[1.1.0.0<sup>2,4</sup>]butane,<sup>4</sup> makes available one more of the "platonic" hydrocarbons for photoelectron-spectroscopic investigation, the only previous example being cubane.<sup>5,6</sup> The compound **3** rearranges ther-



mally to the isomer tetra-*tert*-butylcyclobutadiene,<sup>3</sup> the only known stable tetrasubstituted derivative of the parent hydrocarbon **4**<sup>7</sup> which exhibits statistically averaged  $D_{4h}$  symmetry.

## Experimental Results

In Figures 1 and 2 are shown the photoelectron spectra of **3**, **6**, and the tricyclic hydrocarbon **9**,<sup>8</sup> which is closely related to **4**. The spectra have been recorded on a Turner-type<sup>9</sup> PS 18 spectrometer (Perkin-Elmer, Ltd.) fitted with a  $\pi/\sqrt{2}$  electrostatic analyzer, using He(I $\alpha$ ) radiation, by accumulating the individual runs on a PDP-9 computer acting as a multi-channel analyzer with 2000 channels (sweep range 12–24 eV; sweep frequency  $1 \text{ s}^{-1}$ ; accumulation time of the order of 10 min to 0.5 h). The sample temperatures were 65, 85, and 110 °C for **3**, **6**, and **9**, respectively. The spectra were internally calibrated with rare-gas mixtures.

The ionization energies  $I_j^m$  given in the legends to Figures 1 and 2 refer to the location of the band maxima. For all practical purposes they may be equated to the vertical ionization energies:  $I_j^m \approx I_j^v$ .

As is evident from Figures 1 and 2 the photoelectron spectra of the compounds **3**, **6**, and **9** are somewhat disappointing. This was to be expected because the tetrahedrane moiety of **3** or the cyclobutadiene moieties of **6** and **9** are wrapped by four *tert*-butyl groups, which increase the molecular weights about fivefold, add a fair amount of flexibility to the molecules, and completely dominate the energy region above 10 eV in the photoelectron spectra. Thus, the only bands which yield usable information are the double-humped band at 8 eV in the photoelectron spectrum of **3** and the two bands near 6 and 9 eV in the spectra of **6** and **9**.

**Tetra-*tert*-butyltetrahedrane.** We begin the discussion by applying to tetrahedrane (**1**) a simple equivalent bond orbital model, which has proved to be rather useful for the rationalization of the photoelectron spectra of saturated (linear, branched, or cyclic) hydrocarbons<sup>10</sup> and of cubane.<sup>6</sup> Numbering the CC and CH bonds of **1** as indicated in Figure 3, we obtain the interaction graph **G** in which the filled and open vertices  $v_\mu$  represent the localized CC and CH bond orbitals  $\lambda_{CC}$  and  $\lambda_{CH}$ , respectively. The solid edges of **G** correspond to the geminal  $\lambda_{CC}$ ,  $\lambda_{CH}$  interactions and the dotted ones to the geminal  $\lambda_{CC}$ ,  $\lambda_{CH}$  interactions. Diagonalization of the adjacency matrix  $A(\mathbf{G}) = (a_{\mu\nu})$  yields characteristic values  $x_j$  belonging to the relevant irreducible representations of the group

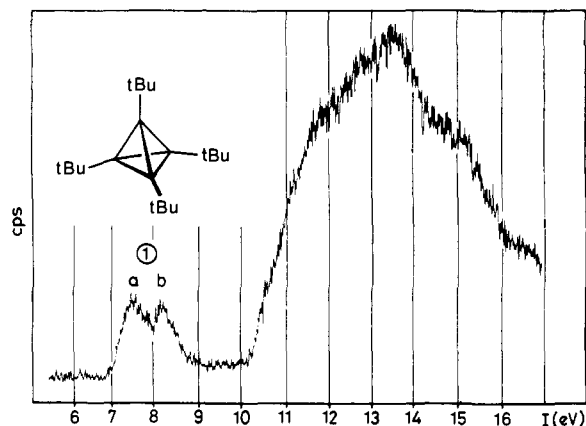


Figure 1. He(I $\alpha$ ) photoelectron spectrum of tetra-*tert*-butyltetrahedrane (3). Band ①:  $I_1(a) = 7.5_0$ ;  $I_1(b) = 8.2_0$  eV.

Table I. Molecular Orbital Energies (eV) for Tetrahedrane (1)

ref	13 <sup>a</sup>	14	15	15
$R_{CC}$ , pm	153.4	156	147.2	148.2
$R_{CH}$ , pm	109.3	107	106.9	105.4
method	MINDO/2	ab initio <sup>b</sup>	STO-3G	STO 4-31G
1e	-9.58	-10.35	-7.76	-9.12
3t <sub>2</sub>	-11.72	-15.34	-13.47	-14.59
3a <sub>1</sub>	-14.90	-20.22	-18.18	-19.35
2t <sub>2</sub>	-18.68	-22.74	-20.74	-21.88
2a <sub>1</sub>		-34.45	-33.74	-35.54

<sup>a</sup> Orbital assignment inferred from degeneracy. <sup>b</sup> Basis: cf. ref 16.

$T_d$ , and thus the model orbital energies  $\epsilon_j = A + Bx_j$ . The parameter  $A$  is the self-energy for the localized orbitals  $\lambda_{CC}$  and  $\lambda_{CH}$  (assumed to be equal, cf. ref 10) and  $B$  is the interaction matrix element for geminal pairs. Note that this model yields only the highest occupied molecular orbitals of C2p, C2s, and H1s parentage. The resulting orbital diagram is shown in the following qualitative scheme, in which the orbital energy spacings are not to scale:

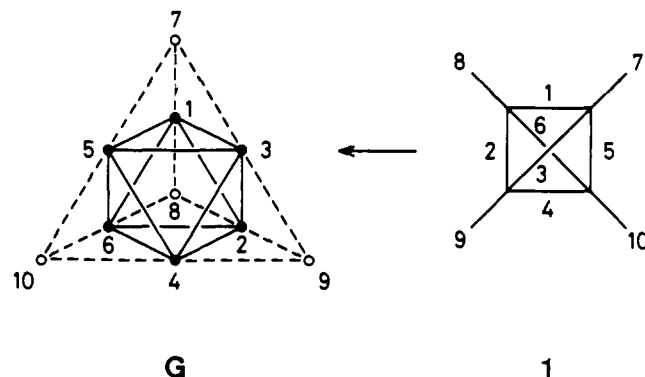
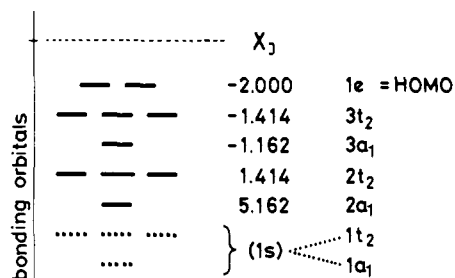


Figure 3. Equivalent bond orbital model for tetrahedrane (1). The graph G lists all geminal interactions, i.e., solid edges = CC,CC interaction, broken edges = CC,CH interactions.

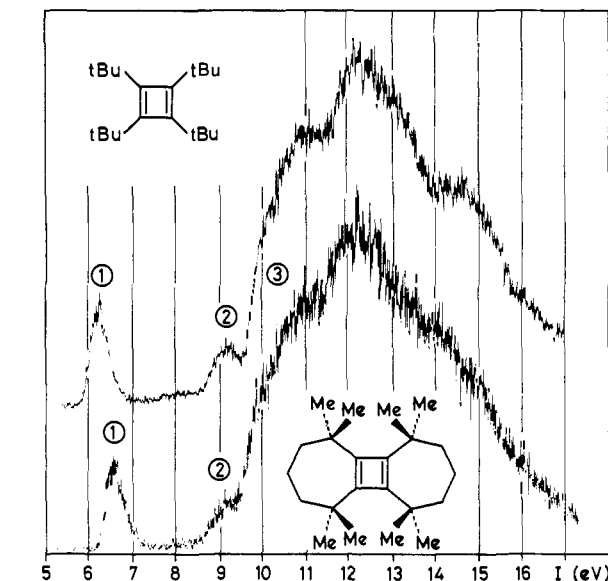


Figure 2. He(I $\alpha$ ) photoelectron spectra of tetra-*tert*-butylcyclobutadiene (6) and of the tricyclic cyclobutadiene derivative 9. 6: ① 6.3<sub>5</sub>; ② 9.2<sub>0</sub>; ③ shoulder ~10.1 eV (onset 9.5 eV). 9: ① 6.6<sub>0</sub>; ② 9.1<sub>5</sub>; ③ shoulder ~10 eV. Orbital type  $\pi$ ,  $\sigma$ , and  $\pi$ , respectively.

(The 1a<sub>1</sub> and 1t<sub>2</sub> orbitals of 1s parentage are not part of this model.) The HOMO 1e is a linear combination of the  $\lambda_{CC}$  only. For this reason it is expected that removal of an electron to yield ground-state 1<sup>+</sup> will result in a pronounced Jahn-Teller distortion of this radical cation and thus in a typical double-humped band in the photoelectron spectrum of 1.<sup>11,12</sup> According to previous experience (cf. the detailed discussion given by Haselbach et al.<sup>12</sup>) a separation of 0.7 eV between the two maxima of the Jahn-Teller band is expected, the maximum at lower energy being the one of greater intensity. This is exactly what is observed in the photoelectron spectrum of 3, as shown in Figure 1. Although there is no longer any doubt that the hydrocarbon described in ref 3 has indeed the structure 3, notwithstanding some of its unexpected properties, the photoelectron spectrum shown in Figure 1 provides an additional, unambiguous proof.

Previous results of molecular-orbital computations<sup>13-15</sup> for the parent compound 1 are collected in Table I. In all cases the orbital sequence obtained is identical with the one given in the scheme, i.e., deduced from the naive equivalent bond orbital treatment<sup>10</sup> discussed above. This agreement is not surprising, because in this highly symmetrical molecule the order of orbitals is completely determined by symmetry and by the nodal properties of the orbitals.

The different treatments yield predictions for the lowest ionization energies which range over 2 eV, which is not unexpected, given the large differences calculated for the equilibrium geometries of 1 by energy minimization within each model. Thus Baird and Dewar<sup>13</sup> predict 9.6 eV for the centroid of the first band, Buenker and Peyerimhoff<sup>14</sup> 10.4 eV, whereas Schulman and Venanzi<sup>15</sup> obtain 8.2 eV, using a scaling factor of -0.9.

An estimate of the influence of the four *tert*-butyl groups of 3 on the position of the first band in its photoelectron spectrum is rather uncertain. The analysis of alkyl-substituted systems (for a summary and further references see a recent review<sup>17</sup>) suggests that substitution of the four hydrogen atoms in 1 by four *tert*-butyl groups will lead to a reduction of the ionization energy by about 1.4-1.7 eV. This, together with the position at 7.9 eV of the centroid of the first band in the photoelectron spectrum of 3 (cf. Figure 1), leads to an estimate of

**Table II.** Molecular Orbital Energies (eV) for Tetramethyltetrahedrane (**2**), Calculated by the STO-3G and the SPINDO Procedures<sup>a</sup>

orbital	STO-3G	SPINDO
2e	-6.23	-8.76
6t <sub>2</sub>	-11.32	-11.51
1t <sub>1</sub>	-14.33	-13.94
5t <sub>2</sub>	-14.51	-14.30
1e	-14.80	-14.43
5a <sub>1</sub>	-14.83	-14.65
4t <sub>2</sub>	-18.15	-16.78
4a <sub>1</sub>	-24.82	-22.59
3t <sub>2</sub>	-25.41	-22.69
3a <sub>1</sub>	-32.30	-27.62

<sup>a</sup> Geometry:  $R_{CC} = 151$  pm;  $R_{CCH_3} = 154$  pm;  $R_{CH} = 109$  pm; all angles at the methyl groups  $109.5^\circ$ . See W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).

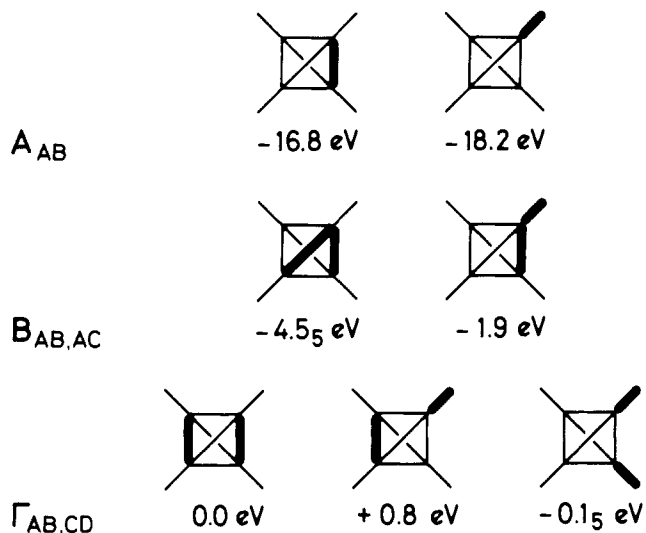
9.3–9.6 eV for the first ionization energy of **1**, in essential agreement with the MINDO/2 result.<sup>13</sup>

Assuming that the *tert*-butyl groups affect all orbital energies of the tetrahedrane moiety roughly to the same extent, we deduce from the photoelectron spectrum of **3** that the gap between the orbital energies of 1e and 3t<sub>2</sub> must be at least ~3 eV, presumably larger. Whereas the ab initio calculations predict ~5–6 eV, the MINDO/2 result of 2.1 eV<sup>13</sup> is certainly too small. However, the crowding of the orbitals subjacent to the HOMO is a well-known artifact of this treatment.

In Table II are reported the orbital energies for the model compound tetramethyltetrahedrane (**2**), calculated both by the SPINDO<sup>18</sup> and the STO-3G<sup>19</sup> procedures.  $T_d$  symmetry and standard bond lengths<sup>20</sup> have been assumed, with the exception of the bond lengths within the tetrahedrane moiety, which have been set equal to 151 pm.

Because SPINDO has been calibrated on ionization energies, the position of the centroid of the first band in the photoelectron spectrum of **2** can be predicted to be  $I_1^c(\mathbf{2}) \approx 8.8$  eV by applying Koopmans' theorem directly to the 2e orbital energy listed in Table II. On the other hand, the STO-3G results have to be used in conjunction with a scaling regression ( $-\epsilon_j^{\text{STO-3G}} = -4.338 + 1.310I_j$ ) derived previously,<sup>10</sup> yielding  $I_1^c(\mathbf{2}) \approx 8.1$  eV. The influence of an alkyl substituent can be mimicked in a first approximation by a shift  $\delta\alpha$  of the Coulomb integrals  $\alpha(2s)$  and  $\alpha(2p)$  at the substituted carbon centers. As a result, the self-energies of all the localized CC orbitals  $\lambda_{CC}$  will be shifted by the same amount and, because the HOMO 1e of **1** is strictly localized on the CC bonds only, the same shift will be experienced by this particular orbital. It has been observed that the ionization energy reducing effect of a methyl group  $\delta\alpha(\text{Me})$  is about 0.5 eV smaller than that of a *tert*-butyl group  $\delta\alpha(t\text{-Bu})$ ,<sup>17</sup> and therefore the experimental value  $I_1^c(\mathbf{3}) = 7.9$  eV extrapolates to  $I_1^c(\mathbf{2}) = 8.4$  eV, which is halfway between the two computed ionization energies given above. Both treatments predict a large gap between the 2e and the 6t<sub>2</sub> band (2.8 eV, SPINDO; 3.9 eV, STO-3G), again in qualitative agreement with the observation for the homologue **3**. The quantitative lack of agreement between the two treatments is certainly due in part to the fact that they have not been adapted to such a highly strained system. In the case of SPINDO the calibration space does not include such molecules and in STO-3G the basis functions do not allow realistic modeling of bond angles smaller than  $\sim 90^\circ$ , quite apart from the fact that the standard CC bond length used for the tetrahedrane nucleus is definitely too large.

As in previous photoelectron spectroscopic investigations of hydrocarbons,<sup>6,10</sup> the canonical molecular orbitals (see Table II) were subjected to a unitary transformation to yield localized orbitals. The localization criterion of Foster and



**Figure 4.** Self-energies  $A_{AB}$  and geminal ( $B_{AB,AC}$ ) and vicinal ( $\Gamma_{AB,CD}$ ) interaction terms between localized band orbitals  $\lambda_{AB}$ ,  $\lambda_{AC}$ , or  $\lambda_{CD}$  obtained from an STO-3G model of tetrahedrane (**1**).

Boys<sup>21</sup> was used for the STO-3G models of **1** and **2**, and that of Edmiston and Ruedenberg<sup>22</sup> for the SPINDO model of **2**. In the following the self-energies of a localized orbital  $\lambda_{AB}$  (i.e., centered on bond AB) are labeled  $A_{AB}$  and the interaction cross terms between two localized orbitals are  $B_{AB,AC}$  for geminal pairs  $\lambda_{AB}$ ,  $\lambda_{AC}$  and  $\Gamma_{AB,CD}$  for vicinal pairs  $\lambda_{AB}$ ,  $\lambda_{CD}$  linked by the bond AC. In Figure 4 we report the results for the STO-3G model of the parent compound **1** computed under the assumption of the minimum energy geometry obtained by Schulman and Venanzi<sup>15</sup> reported in Table I.

To begin with, the self-energy  $A_{CC} = -16.8$  eV for the STO-3G model of **1** is close to the corresponding values  $A_{CC} = -16.9$  eV obtained for cyclopropane<sup>6,23</sup> and cubane,<sup>6,23</sup> and the self-energy  $A_{CH} = -18.2$  eV should be compared to  $A_{CH} = -17.2$  eV in the cyclopropane or  $A_{CH} = -17.3$  eV in the cubane STO-3G model.<sup>6,23</sup> The geminal interaction term  $B_{CC,CC} = -4.55$  eV is only slightly smaller than  $B_{CC,CC} = -4.7$  eV found for cyclopropane but larger (in absolute value) than  $B_{CC,CC} = -3.4$  eV in cubane, because of the smaller CC,CC angle. Also the values  $B_{CC,CH} = -1.9$  eV in **1** and  $B_{CC,CH} = -2.5$  eV in cyclopropane and in cubane show the expected trend. With respect to the vicinal interaction terms it is noteworthy that  $\Gamma_{CC,CC}$  is (practically) zero in the model of **1**, whereas it is very large ( $\Gamma_{CC,CC} = -1.9$  eV) in cubane. Again this is in agreement with previous experience.  $\Gamma_{AB,CD}$  for two vicinal localized orbitals  $\lambda_{AB}$ ,  $\lambda_{CD}$  linked by a bond AC is strongly dependent on the relative conformation of the bonds AB, CD. For a synplanar conformation (twist angle  $\phi = 0^\circ$ ) it is large and negative, whereas for the antiplanar conformation ( $\phi = 180^\circ$ ) it is large and positive. Thus it vanishes for an intermediate angle and it so happens that this is the case for  $\phi = 70.5^\circ$  (i.e., the supplement to the tetrahedral angle of  $109.5^\circ$ ), which is the twist angle of two opposed CC bonds in **1**.

Lengthening a CC bond shifts its self-energy  $A_{CC}$  toward higher values. This is the reason why the assumption of (too long) standard values of 151 pm in the models for **2** (SPINDO and STO-3G) yields  $-14.8$  and  $-15.7$  eV, respectively. However, in both cases it is observed that  $\Gamma_{CC,CC}$  also vanishes, which supports the explanation given above in terms of the twist angle between the two respective CC bonds.

**Tetra-*tert*-butylcyclobutadiene.** The continued interest in the geometry and multiplicity of ground-state cyclobutadiene (**4**) has resulted in an appreciable number of theoretical investigations.<sup>16,24,32</sup> However, few authors have seen fit to list

the orbital energies obtained by their respective calculations.

Several photoelectron spectroscopic investigations of variously substituted cyclobutadienes have appeared, namely, of tri-*tert*-butylcyclobutadiene (**7**),<sup>25</sup> of the dithia derivative **8**,<sup>26</sup> of tri-*tert*-butylcyclobutadiene carboxylate (**10**),<sup>27</sup> and of 1,3-bis(diethylamino)-2,4-bis(ethoxycarbonyl)cyclobutadiene (**11**).<sup>28</sup> The latter two compounds, **10** and **11**, possess ester groups which complicate the photoelectron spectra and in **11** the electronic structure of the butadiene moiety is strongly distorted due to the “push-pull” mechanism.<sup>29</sup>

In the case of **7**, the presence of dimeric material and precursor precluded all but the determination of the first ionization energy, for which Schweig and co-workers found  $I_1^m = 6.83$  eV.<sup>25</sup> Comparison with the corresponding value  $I_1^m = 6.33$  eV of **6** (see Figure 2) shows that replacement of the hydrogen atom in **7** by a fourth *tert*-butyl group shifts the first band by  $-0.50$  eV. This is what one would have expected from the photoelectron spectroscopic investigation of alkyl-substituted ethylenes by Mouvier et al.<sup>30</sup> (For example, the ionization energies of *trans*-1,2-di-*tert*-butylethylene (8.74 eV) and 1,2,3-tri-*tert*-butylethylene (8.17 eV) are separated by 0.6 eV. See also ref 31.) Assuming that each *tert*-butyl group of **6** or each end of the alkyl moieties in **9** contributes a shift of  $-0.50$  eV, an ionization energy  $I_1^m = 8.3$  eV is predicted for the unsubstituted parent compound **4**, a value which may well be uncertain by  $\pm 0.2$  eV. Thus it is in essential agreement with the predicted value of 8.65 eV (*ab initio*) calculated by Buenker and Peyerimhoff,<sup>16</sup> and the LNDO/S value of 8.19 eV obtained by Schweig and his co-workers<sup>32</sup> for the ionization energy of **4**. More recently Worley et al.<sup>33</sup> have derived an estimate of 8.29 eV for the first ionization energy of **4** from a study of the photoelectron spectrum of its tricarbonyl complex, a value in complete agreement with the one obtained above.

The first ionization energy of the tetramethyl derivative **5** is expected to lie about halfway between those of **4** and **6**, i.e., near 7.3 eV. We have carried out *ab initio* STO-3G<sup>19</sup> and SPINDO<sup>18</sup> calculations for **5** using a standard geometry<sup>20</sup> and an *ab initio* STO-3G calculation with partial geometry optimization, i.e., keeping all structural parameters standard, except the single- and double-bond distances within the four-membered ring. The results for the first ionization energy are as follows:  $I_1$  (STO-3G; std geom) = 6.5,  $I_1$  (SPINDO; std geom) = 8.1,  $I_1$  (STO-3G; part opt geom) = 7.1 eV. (The STO-3G values are derived from the respective orbital energies ( $-4.14$  and  $-4.98$  eV) using the scaling function given above.) The STO-3G value obtained by partial geometry optimization is in fair agreement with our experimentally based estimate. However, comparing the two STO-3G values shows how sensitive the computed value is to small changes in the structural parameters. Notwithstanding such quantitative uncertainties there is absolutely no doubt that the first band in the photoelectron spectra of **6** and **9** (and thus of **7** and **8**) is due to the removal of an electron from a  $b_{3g}(\pi)$  orbital.

The photoelectron spectra of **6**, **8**,<sup>26</sup> and **9** exhibit a broad, second band at  $I_2^m \approx 9.2$  eV, if we neglect the strong band at 8.2 eV in the spectrum of **8**, which is due to the ejection of an electron from one or the other of the sulfur lone pair orbitals. This broad band was assumed by Schweig and co-workers<sup>26</sup> to be due to a secondary product, although no further comments concerning this were made. The fact that the same band occurs in all three spectra (i.e., of **6**, **8** and **9**) indicates that it is an intrinsic component due to the cyclobutadiene moiety. All theoretical treatments carried out so far agree that the ordering of the three highest occupied molecular orbitals of the parent compound **4** should be  $b_{3g}(\pi) \equiv \text{HOMO}$ ,  $b_{3u}(\sigma)$ ,  $b_{2u}(\pi)$ . The same sequence has been obtained in the calculations for the tetramethyl derivative **5** mentioned above, independent of the treatment used (STO-3G or SPINDO) or

whether a standard or an optimized geometry was assumed.

Thus, according to theory the broad band near 9.2 eV is probably due to the removal of an electron from a  $\sigma$  orbital localized within the cyclobutadiene moiety. Indirect support for such a high-lying  $\sigma$  orbital can be found in the photoelectron spectroscopic results for 4-radialene.<sup>34</sup> For this molecule a ring  $\sigma$  orbital was found to exhibit an ionization energy of 10.8 eV despite the fact that eight  $sp^2$ -hybridized centers are found in the molecule. When one considers inductive effects and the fact that the higher lying orbitals of the *tert*-butyl groups would hyperconjugate more effectively than the  $\sigma$  system of the exocyclic double bonds, it is quite reasonable that a  $\sigma$  orbital could exhibit such a low ionization energy.

The location of the third band which should be due to the ejection of an electron from the  $b_{2u}(\pi)$  orbital which is essentially the in-phase combination of the two double-bond  $\pi$  basis functions is a difficult problem, because the spectral region above 10 eV is completely dominated by the band system due to the large alkyl moieties of **6** and **9** (see Figure 2). In previous investigations of alkyl-substituted acetylenes<sup>35,36</sup> it has been shown that the band system due to an alkyl group R in the photoelectron spectrum of a substituted acetylene is superposable with that of the corresponding alkane RH, except for a small, uniform shift of the system which in the case of the acetylenes is of the order of 0.5–0.7 eV (to higher ionization energies). Assuming this to be also true for **6** and **9** we expect that the onset of the band system due to the *tert*-butyl groups in **6** should lie roughly 0.5 eV higher in energy than the band onset of the isobutane photoelectron spectrum, which occurs at 10.0 eV.<sup>37</sup> As can be seen from Figure 2, there is an additional band in front of the expected system with an onset of 9.5 eV and an estimated maximum near 10.2 (**6**) or 10.0 eV (**9**). It is a fair guess that this band, which is partially overlapped by the alkyl band system, is the one due to electron ejection from the  $b_{2u}(\pi)$  orbital. (Note that the corresponding band in the photoelectron spectrum of **8** (onset 9.5 eV, maximum 10.2 eV) had been assigned by Schweig and co-workers<sup>26</sup> to the  $\sigma$  orbital  $b_{3u}$ , because the feature near 9.2 eV was assumed to be spurious.)

If we accept this assignment, then the energy gap between the two  $\pi$  bands, i.e., those correlated with the two orbitals which are dominated by the in-phase and out-of-phase combination of the two double-bond  $\pi$  basis functions, is approximately 3.9 eV in **6**, 3.3 eV in **8**,<sup>26</sup> and 3.5 eV in **9**. Extrapolating the values observed for the ionization energies of the tricarbonyl complex of the parent compound **4**, Worley et al.<sup>33</sup> predict that the second ionization energy of free **4** should be 11.95 eV, which leads to a value of 3.7 eV for the energy gap between the two  $\pi$  bands of **4**. Assuming that the influence of the substituting alkyl groups has only a small effect on the difference of the two  $\pi$  ionization energies, a value of  $3.6 \pm 0.2$  eV seems a reasonably safe estimate. The LNDO/S results for the parent compound **4**, obtained by Schweig et al.,<sup>32</sup> yield a corresponding gap of  $\sim 5$  eV and our own calculations for the tetramethyl derivative **5** lead to the following values: standard geometry 3.0 (SPINDO), 4.9 eV (STO-3G); optimized geometry 4.0 eV (STO-3G). These results are in good agreement with the ones deduced from the experiment if we take into consideration that they have been computed for the unsubstituted and the methyl-substituted cyclobutadiene. (Note again the significant change of the predicted value for **5** on geometry optimization.)

**Note Added in Proof.** Recently, Schweig and Thiel<sup>38</sup> have published a most interesting and stimulating theoretical analysis of the thermal interconversion **3**  $\rightarrow$  **6**, from which it can be inferred that the isolation of the parent compound **1** should be feasible. Professor Schweig has kindly provided additional information relevant to the present work, for which

we are very grateful. Assuming Koopmans' approximation, his MNDO calculations yield the vertical ionization energies of 9.76 eV for **1** and 8.44 eV for **4** in perfect agreement with the values deduced in this paper ( $9.4_5 \pm 0.2$  and  $8.3 \pm 0.2$  eV, respectively). Although, according to Professor Schweig, the method used in ref 38 is known to underestimate the influence of alkyl groups on ionization energies, it is noteworthy that the MNDO model predicts the orbital sequence  $\pi$ ,  $\pi$ ,  $\sigma$  for the highest three occupied MOs, rather than  $\pi$ ,  $\sigma$ ,  $\pi$  as postulated in this paper. However, the relative sequence of the second  $\pi$  and of the first  $\sigma$  orbital seems to depend in a sensitive way on the assumed geometry of the molecule. If nothing else, this result suggests that our proposed assignment should be accepted with the customary caution.

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