

## 109. The Electronic Spectrum of Tricyclo[3.3.0.0<sup>2,6</sup>]octa-3,7-diene

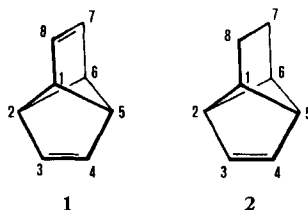
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*Summary.* The unusual electronic spectrum of the title compound is shown to be due to the strong interaction between the  $\pi$ -orbitals of the double bonds and the *Walsh*-orbitals of the four-membered ring.

Recently, *Meinwald & Tsuruta* [1] and also *Zimmermann, Robbins & Schantl* [2] prepared the title compound **1** and tricyclo-[3.3.0.0<sup>2,6</sup>]oct-3-ene (**2**). Both compounds show a remarkable UV.-spectrum for non-conjugated olefins.



For **1**, an absorption at 300 nm is reported with a molar extinction coefficient of 190. For **2**, the first band is shifted to 250 nm with an extinction coefficient of 150.

To understand the UV.-spectra of **1** and **2** we have used the CNDO/1 method [3]. In this procedure the elements of the  $F$ -matrix are given by equations (1) and (2).

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu}) \gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} \quad (1)$$

where

$$U_{\mu\mu} = -I_{\mu} - (Z_A - 1) \gamma_{AA}, \quad (2)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB}.$$

The parameters used by *Pople, Santry & Segal* [3] were calibrated to reproduce the results of *ab initio* calculations for small molecules. For the rationalisation of UV.-spectra certain changes have to be introduced into the CNDO method.

*P. A. Clark & Ragle* [4] used *Pople's* CNDO procedure with different core parameters  $U_{\mu\mu}$  and resonance integrals  $\beta$ . *Del Bene & Jaffé* [5] introduced different  $\beta$ -values for  $\sigma$ - and  $\pi$ -bonds to increase the energy difference between  $\sigma$ - and  $\pi$ -orbitals. They also evaluated the one-centre integrals  $\gamma_{AA}$  empirically and used the extrapolation technique proposed by *Pariser & Parr* [6] to calculate the two-centre integrals  $\gamma_{AB}$ . *D. T. Clark* [7] took  $I_{\mu}$  as the average of the valence-state ionization potentials and the one-centre integrals  $\gamma_{AA}$ , as described by *Sichel & Whitehead* [8], and calculated the two-centre integrals  $\gamma_{AB}$  according to the procedure described by *Ohno* [9]. The resonance integrals  $\beta$  were calculated by the *Mulliken, Wolfsberg & Helmholz* approximation [10]

$$\beta_{\mu\nu} = -0.5 \cdot K \cdot (I_{\mu} + I_{\nu}) \cdot S_{\mu\nu} \quad (3)$$

For  $K$ , an empirical constant, the value 0.78 was used. To calculate the overlap integral  $S_{\mu\nu}$ , *Slater* type orbitals were used with orbital exponents suggested by *Burns* [11].

Our procedure is closely related to that of *D. T. Clark*, but the empirical constant  $K$  (eq. 3) is taken as 1.0, and the orbital exponents are those suggested by *Slater* [12]. This variation of the CNDO/1 method has been tested on a number of smaller molecules and gives satisfactory agreement with the observed UV.-spectra. For the CI treatment only singly excited configurations were used.

Since the geometry of the molecule is not known we assumed  $D_{2d}$  and  $C_{2v}$  symmetry for **1** and **2**, respectively. We choose the following bond lengths for **1**: C(3) – C(4) = 1.34 Å, C(1) – C(2) = 1.53 Å, C(2) – C(3) = 1.54 Å, and all C–H = 1.10 Å. The angle between the planes C(1) – C(2) – C(6) and C(1) – C(5) – C(6) was assumed to be 160°. In **2**, the C(7) – C(8) distance was taken as 1.54 Å.

The results for **1** and **2** are summarized in the table. For **1**, the first two singlet

Calculated singlet transition for **1** and **2** below 6 eV

	transitions	energy (eV)	(nm)	calculated oscillator strength
<b>1</b>	${}^1E \leftarrow {}^1A_1$	4.23	293.0	0.082
	${}^1E \leftarrow {}^1A_1$	5.43	228.3	0.196
	${}^1A_2 \leftarrow {}^1A_1$	5.58	222.1	0.0
<b>2</b>	${}^1B_1 \leftarrow {}^1A_1$	4.48	276.7	0.086
	${}^1B_2 \leftarrow {}^1A_1$	5.89	210.4	0.012
	${}^1A_2 \leftarrow {}^1A_1$	5.89	210.4	0.0

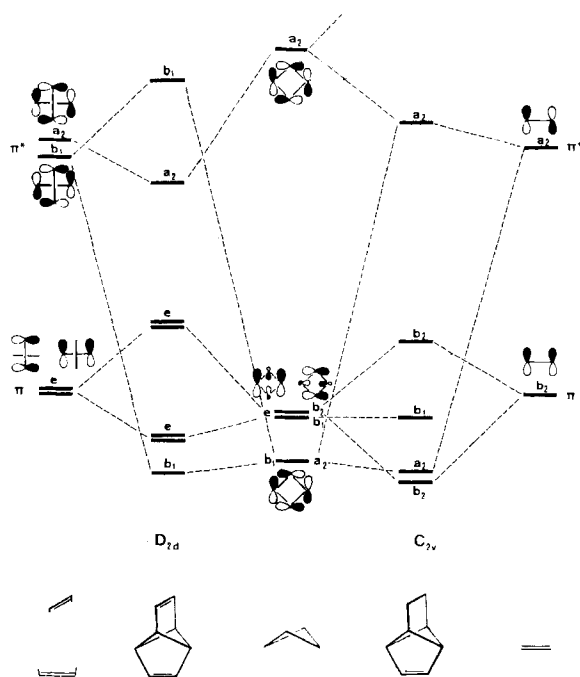
transitions ( ${}^1E \leftarrow {}^1A_1$ ) are allowed. The first involves an  $\mathbf{e}(\pi)$ - and an  $\mathbf{a}_2(\pi^*)$ -orbital, which are respectively raised and lowered in energy because of interaction between the *Walsh*-type orbitals of the cyclobutane ring [13] and the  $\pi$ - and  $\pi^*$ -orbitals of the ethylene units<sup>1)</sup>. The second corresponds to excitation from the highest occupied orbital  $\mathbf{e}(\pi)$  to the orbital  $\mathbf{b}_1(\pi^*)$ . The qualitative interaction diagram between *Walsh*- and  $\pi$ -orbitals (fig.) shows that the two perpendicular  $\pi$ -systems in **1** and the four *Walsh*-orbitals of cyclobutane are ideally arranged for interaction. Mixing gives a pair of high lying occupied orbitals ( $\mathbf{e}$ ) and increases the splitting between the two  $\pi^*$  orbitals.

For **2**, the CNDO-CI calculation predicts three transitions between 200 and 300 nm, of which two are allowed. The first ( ${}^1B_1 \leftarrow {}^1A_1$ ), at 276.7 nm, is essentially a  $\pi^* \leftarrow \pi$  transition, where the  $\pi$ -orbital is mixed with the high lying *Walsh*-orbital of  $B_2$  symmetry (see fig.). The second transition  ${}^1B_2 \leftarrow {}^1A_1$  corresponds mainly to excitation from the *Walsh*-orbital  $\mathbf{b}_1$  to the  $\pi^*$  orbital of the olefinic unit (see fig.).

The forbidden  ${}^1A_2 \leftarrow {}^1A_1$  transitions for **1** and **2** (see table) are from a high lying  $\sigma$ -orbital of  $A_1$  symmetry to the lowest  $\pi^*$ -orbital of  $A_2$  symmetry. According to our CNDO/1 calculations, this  $\sigma$ -orbital lies between the two  $\mathbf{e}$ -orbitals of **1** and below the  $\mathbf{b}_1$  orbital of **2** (see fig.). This might be an artefact of the procedure since all current valence-electron methods yield rather high orbital energies for  $\sigma$  levels [14].

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<sup>1)</sup> Similar results have been derived by *Hoffmann & Davidson*, see [13].



Qualitative interaction diagram between the two perpendicular ethylene units and cyclobutane in **1** (left side) and the ethylene part and cyclobutane in **2** (right side)

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