# cis,trans,cis- and trans,trans,trans-1,2,3,4-Tetravinylcyclobutane — Preparation and Some Spectroscopic Properties

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The title compounds **1** and **2** are prepared using standard procedures. The He(I) PE spectra of **1** and **2** show strong interaction ($\beta = -1.9$ eV) between vinyl groups and the four-membered ring. The through space interaction between the vinyl groups is found to be minute.

### cis,trans,cis- und trans,trans,trans-1,2,3,4-Tetravinylcyclobutan — Darstellung und einige spektroskopische Eigenschaften

Die Titel-Verbindungen **1** und **2** werden mit Hilfe von bekannten Reaktionsfolgen dargestellt. Die He(I) PE-Spektren von **1** und **2** zeigen eine starke Wechselwirkung ($\beta = -1.9$ eV) zwischen den Vinylgruppen und dem Vierring. Die räumliche Wechselwirkung zwischen den Vinylgruppen ist nicht meßbar.

Recently we have studied the through space and the through bond interaction in the different isomeric 1,2- and 1,3-divinylcyclobutanes by means of the He(I) photoelectron spectroscopy[1]. We were able to show that there is quite a large interaction between the π-system and the σ-part of the four-membered ring if the bisected conformation is adopted. In continuation of this research we synthesized *cis,trans,cis-* and *trans,trans,trans-*1,2,3,4-tetravinylcyclobutane (**1**) and (**2**). In addition to the fact that **1** and **2** are closely related to the isomers of 1,2- and 1,3-divinylcyclobutane, **2** also bears some relation to tricyclo[5.5.0.0$^{2,8}$]dodeca-3,5,9,11-tetraene, a molecule for which strong through bond interaction has been proposed[2].
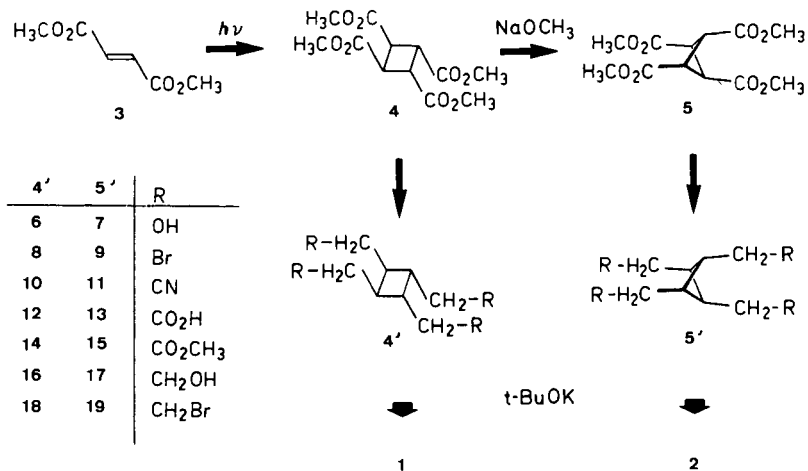


**1**                                   **2**
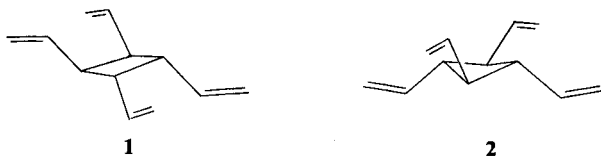
## Synthesis of 1 and 2

Starting point for both compounds is the photodimerization of fumaric ester **3** leading to tetramethyl *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylate (**4**) (see Scheme 1). Variation of the original procedure[3] gives **4** in almost quantitative yield. Isomerization of **4** in the presence of strong base[4] yields **5**, the starting material for **2**. The reduction of **4** and **5** to the corresponding alcohols **6**[5] and **7**[6] is carried out with LiAlH$_4$.

Extension of the side chains using standard operations[3,7] (see Scheme 1) yields the tetrabromides **18** and **19**. Treating the latter compounds with potassium *tert*-butoxide yields **1** and **2** in an overall yield of 15 and 11%, respectively, starting from fumaric ester **3**. **1** is thermally unstable and undergoes two consecutive Cope rearrangements to give cyclododecatetraene[8].

*Scheme 1*

| 4' | 5' | R |
|----|----|-----|
| 6 | 7 | OH |
| 8 | 9 | Br |
| 10 | 11 | CN |
| 12 | 13 | $CO_2H$ |
| 14 | 15 | $CO_2CH_3$ |
| 16 | 17 | $CH_2OH$ |
| 18 | 19 | $CH_2Br$ |

## Conformation of 1 and 2

To elucidate the conformation of **1** and **2** we have minimized the heat of formation of both compounds with respect to the geometrical parameters by using the MINDO/3 method[9,10]. In both cases we find *one* minimum. The geometrical parameters calculated are listed in Fig. 1. All vinyl groups prefer the bisected conformation as encountered in the 1,2- and 1,3-divinylcyclobutanes[1]. In Tab. 1 we have listed the heat of formation of two further conformations of **1** and **2** which were derived by rotating one or all four vinyl groups by 180° starting from the minimum conformations given in Fig. 1. The results demonstrate that the total minimum is shallow with respect to rotation of the vinyl groups.
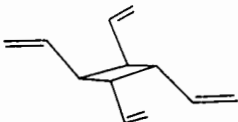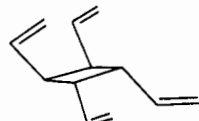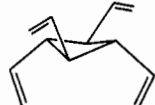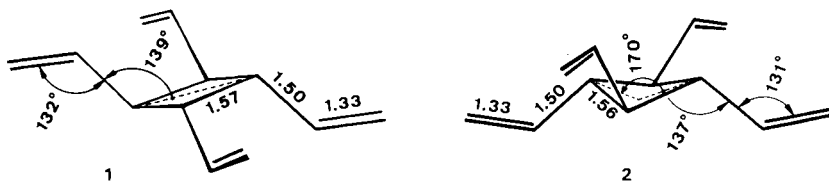
Fig. 1. Geometrical parameters of **1** and **2** according to a MINDO/3 calculation

Table 1. Heat of formation ($\Delta H_f$) of **1** and **2** together with two other conformers. All values in kcal/mol

Compound

| $\Delta H_f$ | 88.7 | 91.0 | 96.5 |
|---|---|---|---|

| $\Delta H_f$ | 86.2 | 89.5 | 93.1 |
|---|---|---|---|

## PE Spectra of 1 and 2

The He(I) photoelectron (PE) spectra of **1** and **2** are shown in Figure 2. The relevant vertical ionization potentials are collected in Table 2. Both spectra are very similar, showing two close lying peaks (bands ①, ②, and ③, ④) below 10 eV as anticipated from the PE spectra of various isomeric divinylcyclobutanes[1]. The close similarity between both spectra indicates that the spacial interactions between the vinyl groups are small and other interactions dominate.

Table 2. Comparison between the first PE bands of **1** and **2** and calculated orbital energies. All values in eV

| Com-pound | Band | $I_{v,j}$ | Assign-ment | $-\varepsilon$ (ZDO) | $-\varepsilon$ (ZDO + J.T.) | $-\varepsilon$ (MINDO/3) | $-\varepsilon$ (MNDO) |
|---|---|---|---|---|---|---|---|
| **2** | ① | 9.02 | 8e | 9.24 (e) | 9.04 (e) | 9.13 ($2b_1(\pi)$) | 9.50 ($2b_1(\pi)$) |
| | ② | 9.25 | $2b_1$ | 9.27 ($b_1$) | 9.27 ($b_1$) | 9.32 ($8e(\pi)$) | 9.95 ($8e(\pi)$) |
| | ③ | 9.90 | 8e | 9.90 ($a_2$) | 9.44 (e) | 10.45 ($1a_2(\pi)$) | 10.28 ($1a_2(\pi)$) |
| | ④ | | $1a_2$ | 11.26 (e) | 9.90 ($a_2$) | 10.41 ($7a_1$) | 11.80 ($7a_1$) |
| | ⑤ | 10.8 | | 12.73 (e) | 11.06 (e) | 11.0 (7e) | 11.93 (7e) |
| | ⑥ | | | | 11.46 | | |
| **1** | ① | 9.16 | $8a_u$ | 9.24 ($a_u$) | 9.04 ($a_u$) | 9.17 ($9a_g(\pi)$) | 9.57 ($9a_g(\pi)$) |
| | ② | 9.38 | $9a_g$ | 9.24 ($b_u$) | 9.27 ($a_g$) | 9.29 ($8a_u(\pi)$) | 9.87 ($8b_u(\pi)$) |
| | ③ | 9.74 | $8b_u$ | 9.27 ($a_g$) | 9.44 ($b_u$) | 9.37 ($8b_u(\pi)$) | 9.98 ($8a_u(\pi)$) |
| | ④ | 9.90 | $7b_g$ | 9.90 ($b_g$) | 9.90 ($b_g$) | 10.38 ($7b_g(\pi)$) | 10.17 ($7b_g(\pi)$) |
| | ⑤ | 10.8 | $7a_u$ | 11.26 ($a_u$) | 11.06 ($a_u$) | 10.25 ($7a_u$) | 11.56 ($7a_u$) |
| | ⑥ | 11.1 | $7b_u$ | 11.26 ($a_u$) | 11.46 ($b_u$) | 10.91 ($6b_g$) | 11.90 ($6a_u$) |

To interprete the spectra we rely on the validity of Koopmans' theorem $(-\varepsilon_j = I_{v,j})$[11]. To derive the orbital energies we used a ZDO model and semiempirical calculations of the MINDO/3[9] and MNDO[12] type.
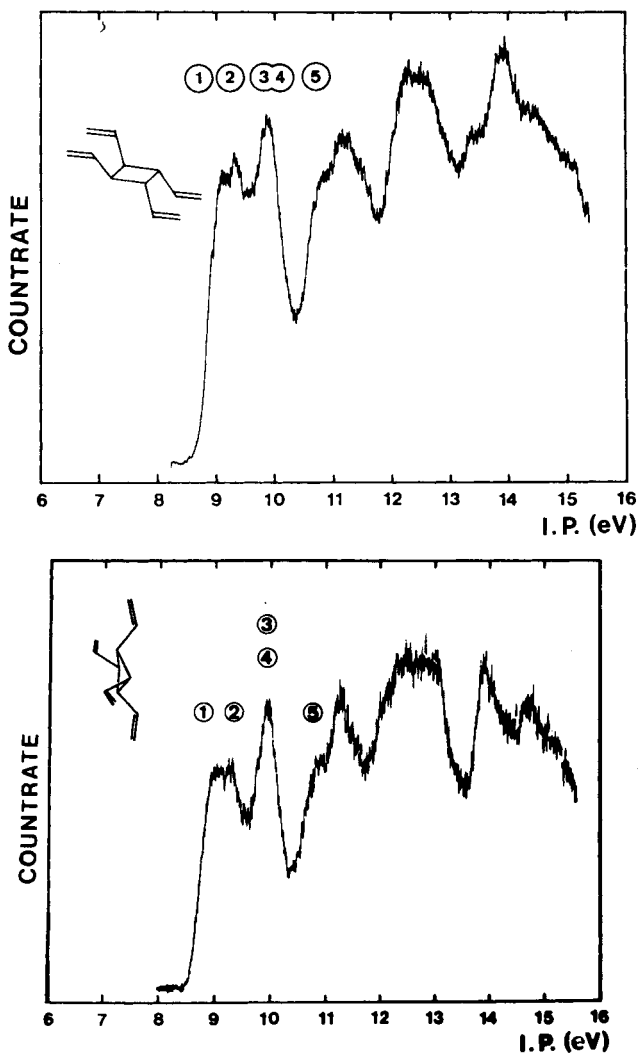


Fig. 2. He(I) PE spectra of **1** and **2**

## ZDO Model

In our ZDO model we have to assess the basis orbital energies of the vinyl groups and of the Walsh orbitals of the four-membered ring. For the vinyl group we choose $-9.9\,\text{eV}$ by correcting the first ionization potential of propene (9.73 eV[13]) due to the hyperconjugation effect of a further alkyl group.

For the basis orbital energies of the four-membered ring we choose $\alpha(\Phi_1) = \alpha(\Phi_2) =$ $-10.6$ eV and $\alpha(\Phi_3) = -12.1$ eV. These values are derived from the first ionization potentials of the cyclobutane ring ($I_{v,1} = 11.0$ and $I_{v,2} = -12.5$ eV[14]) correcting it for the inductive effect of each vinyl group by 0.1 eV. In line with this choice are earlier investigations on cyclobutane derivatives[15-17]. As resonance integral between the 2p AO's of the four-membered ring and the double bond we adopt $\beta = -1.9$ eV[1,15-17]. With this value the following matrix elements are calculated:

$$H_{\pi,\sigma}(a_g) = H_{\pi/\sigma}(b_1) = -1.34 \text{ eV}$$
$$H_{\pi/\sigma}(e) = -0.95 \text{ eV}$$

Solving the sekular determinants with these values yields the orbital energies listed in column 5 of Table 2. In Figure 3 the three highest occupied σ-orbitals of the four-membered ring are shown in the *Walsh*[18] and *Salem*[19] presentation as well as the four linear combinations resulting from the four π-orbitals of the vinyl groups. From this comparison it is seen that all three σ-orbitals may interact with the π-system. Only one π-molecular orbital ($a_2$ in point group $D_{2d}$ and $b_g$ in point group $C_{2h}$) has no partner to interact with. We expect the corresponding band to occur at 9.9 eV, the basis orbital energy of a noninteracting vinyl group at the four-membered ring.
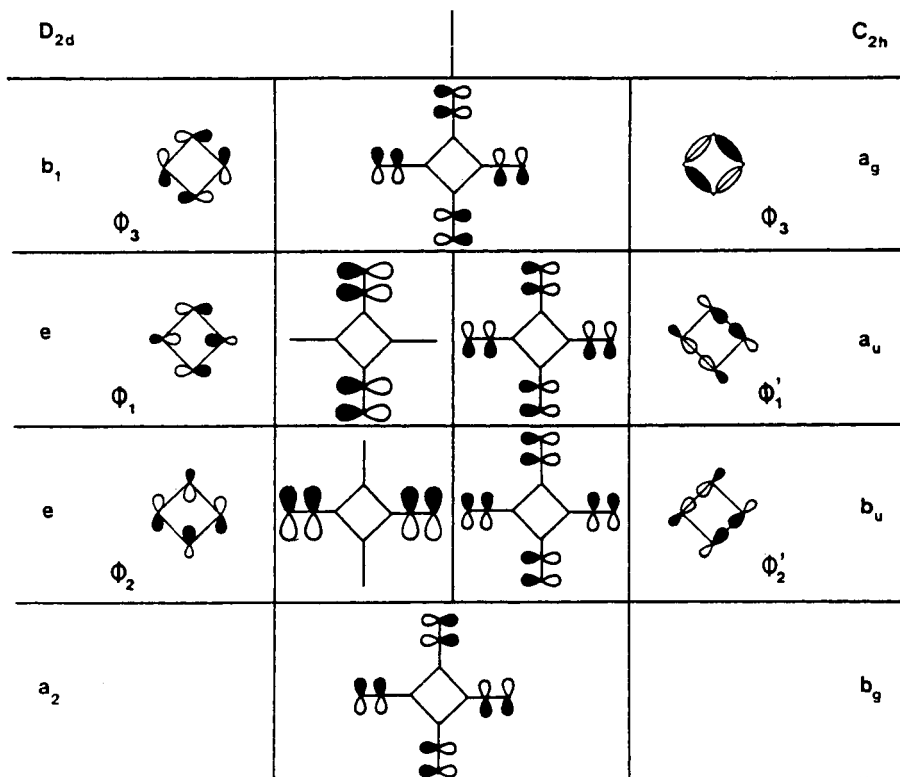


Fig. 3. Representation of the highest occupied σ-orbitals of the four-membered rings in **1** and **2** according to *Walsh*[18] (left) and *Salem*[19] (right) together with the four linear combinations resulting from the π-orbitals of the vinyl groups

In Figure 4 an interaction diagram based on the ZDO model for **1** and **2** is given. On the left of this Figure we show the basis orbital energies of the cyclobutane unit and on the right those of the four vinyl groups.
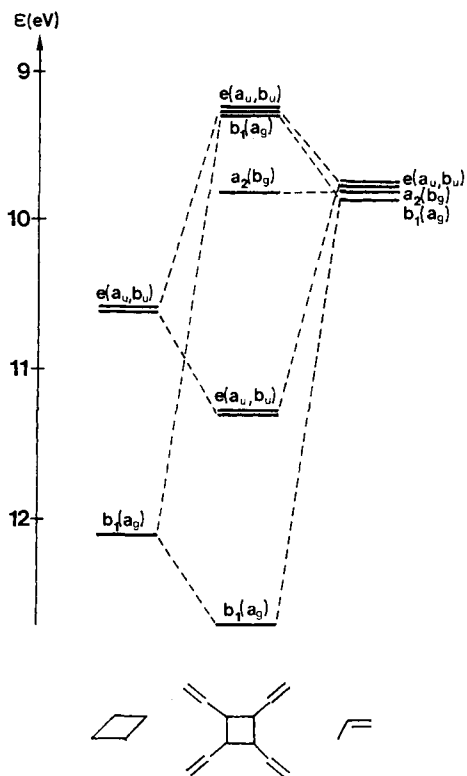


Fig. 4. Diagram for the interaction of the four vinyl groups in **1** and **2** and the Walsh orbitals. The irreducible representations refer to **1** ($D_{2d}$ group) and **2** ($C_{2h}$ group, given in parantheses)

To interprete the PE spectra we have to consider a Jahn-Teller split for the bands which originate from degenerate orbitals. In case of cyclobutane compounds a value of $0.4 - 0.5$ eV[20] seems reasonable. A similar splitting (pseudo Jahn-Teller effect) is expected for the MO's which belong to the irreducible representations $A_u$ and $B_u$ in the case of **2**. Both corrections are included in column 6 of Tab. 2. Adopting these corrections, the agreement between ZDO results and experiment is satisfactory.

## Semiempirical Calculations

Adopting the predicted equilibrium geometries shown in Fig. 2 for **1** and **2** we have calculated the orbital energies of both compounds using the MINDO/3[9] and MNDO[12] method. Both methods confirm the given assignment (see columns 7 and 8 of Tab. 2) if

we correct the calculated values for 8e as well as $8b_u$ and $8a_u$ by a Jahn-Teller or pseudo Jahn-Teller split of 0.4 eV. This correction yields an excellent agreement between MINDO/3 results and experiment considering the first three bands. The ionization potential for the π-MO which does not interact with any Walsh orbital ($1a_2$ for **1** and $7b_g$ for **2**) is predicted at too high values.

## NMR Spectra of 1 and 2

In Figure 5 we show the ^{1}H NMR spectra of **1** and **2**. The chemical shifts and coupling constants are given in Tab. 3. As anticipated both spectra are very similar due to the same topology. We observe three groups of signals, one at high field (3.0 and 2.4 ppm, respectively) and multiplets around 5 and 6 ppm. The integration yields a ratio of 1:2:1. The multiplets around 5 and 6 ppm we assign to $H^1$, $H^2$ and $H^3$ of the vinyl group (see Table 3). The coupling constants are very similar to those reported for the vinyl group[9]. In case of **2** we find a broad singlet at high field (2.41 ppm) while in the spectrum of **1** a broad doublet (3.00 ppm) is found. The signals are due to the protons bound to the cyclobutane ring. At $-100$°C in $CD_2Cl_2$ no change of the spectra has been observed. The ^{13}C NMR data obtained for **1** and **2** in $CDCl_3$ are summarized in Tab. 4.

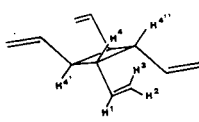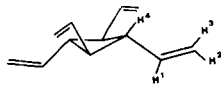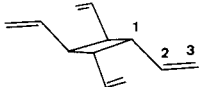Table 3. ^{1}H NMR spectral data of **1** and **2** (300 MHz; $CDCl_3$, TMS) δ values in ppm

| Compound | δ(4H) | | J(Hz) | |
|---|---|---|---|---|
| | $H^1$ | 5.93 | $J_{1,2}$ | 10.6 |
| | $H^2$ | 5.06 | $J_{1,3}$ | 16.8 |
| | $H^3$ | 5.04 | $J_{2,3}$ | 1.8 |
| | $H^4$ | 3.00 | $J_{1,4}$ | 4.9 |
| | | | $J_{1,4'}$ or $J_{1,4''}$ | 0.9 |
| | $H^1$ | 5.86 | $J_{1,2}$ | 10.2 |
| | $H^2$ | 4.98 | $J_{1,3}$ | 17.3 |
| | $H^3$ | 5.04 | $J_{2,3}$ | 1.7 |
| | $H^4$ | 2.41 | $J_{1,4}$ | 0.7 |

Table 4. ^{13}C NMR spectral data of **1** and **2** (72.46 MHz; $CDCl_3$, TMS). δ values in ppm

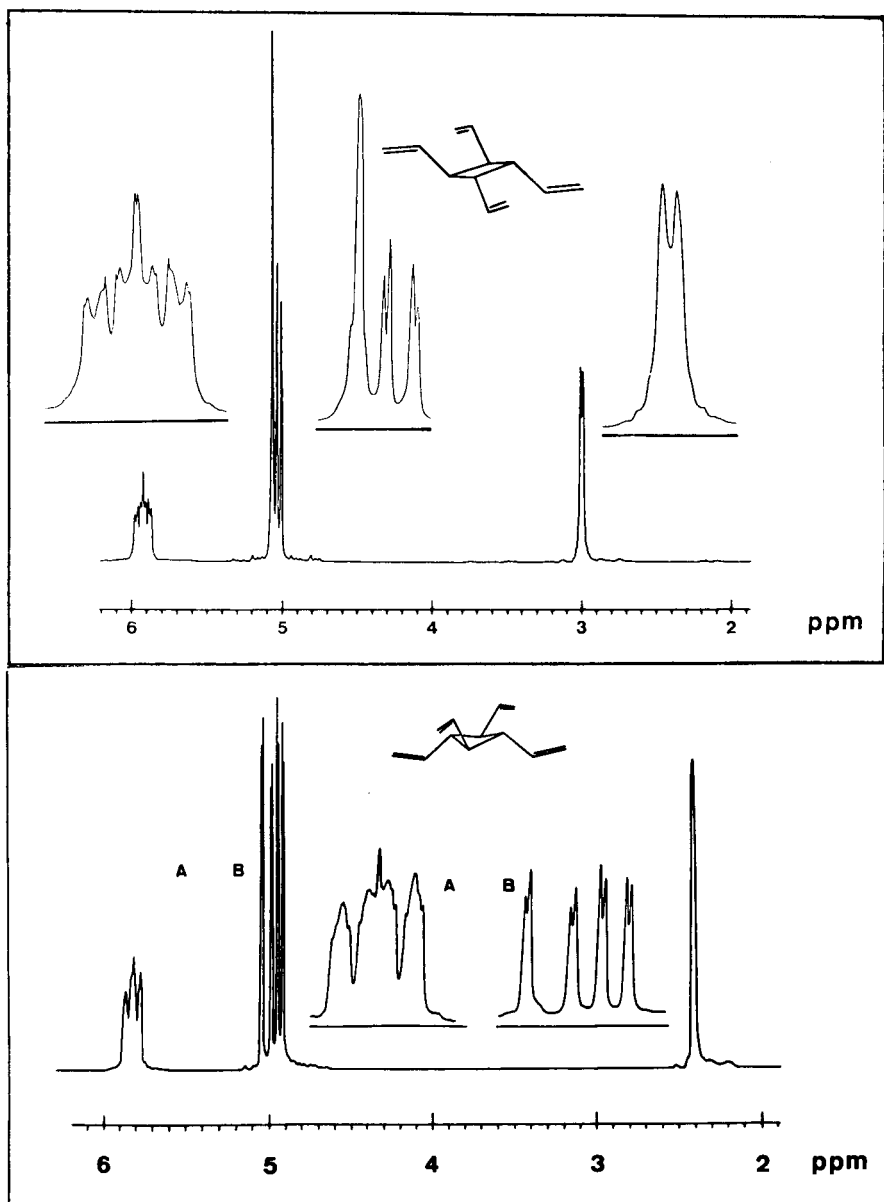| Atom | | |
|---|---|---|
| 1 | 138.3 (d) | 140.2 (d) |
| 2 | 115.0 (t) | 114.4 (t) |
| 3 | 45.3 (d) | 48.9 (d) |

Fig. 5. $^1$H NMR spectra (300 MHz) of **1** and **2** in CDCl$_3$ at 25 °C

## Final Remarks

Our investigations on **1** fully confirm earlier results obtained with *anti*-tricyclo-[6.4.0.0$^{2,7}$]dodeca-3,5,9,11-tetraene (**20**)[16)] for which a strong interaction between the two diene moieties mediated by the four-membered ring has been encountered. Further-

more the results on **2** are on line with earlier predictions on tricyclo[5.5.0.0$^{2,8}$]dodeca-3,5,9,11-tetraene (**21**)[2]. In this case also strong interaction of the two diene moieties on opposite sides of the four-membered ring is predicted.
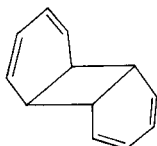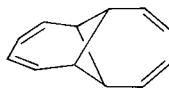


**20**                                        **21**

As seen from Fig. 3 the two vinyl groups on opposite sides of the four-membered ring in **1** and **2** interact very strongly via the relay of the Walsh orbitals.

## Experimental Part

Melting points: uncorrected. − $^1$H NMR: Varian EM 360 (60 MHz), EM 390 (90 MHz), and Bruker WM 300 (300 MHz) spectrometers. − $^{13}$C NMR: Bruker WM 300, 75.46 MHz. − Mass spectra: ZAB instrument from Vacuum Generators. − Preparative gas chromatography: Perkin Elmer F 21, FID, column (18% SE 30 on chromosorb W-AW DLMS, length 4 m, diameter 12 mm, flow 300 ml N$_2$/min). − Elementary analyses: Mikroanalytisches Labor der Chemischen Institute der Universität Heidelberg. − PE spectra: PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England). The calibration was done with Ar and Xe, a resolution of 20 meV on the $^2P_{3/2}$Ar was achieved.

*Tetramethyl cis,trans,cis-1,2,3,4-Cyclobutanetetracarboxylate* (**4**): A vigorously stirred suspension of 111.4 g (0.77 mol) of dimethyl fumarate[21] in 5 l of water in an open glass beaker is irradiated for 2 days with a TQ-150 lamp (Quarzlampengesellschaft, Hanau) through a water-cooled quarz immersion finger. The product is filtered, washed with water, and dried. Yield 106 g (95%), m. p. 144 − 145 °C[3].

*cis,trans,cis-1,2,3,4- and trans,trans,trans-1,2,3,4-Tetrakis(bromomethyl)cyclobutane* (**8** and **9**): 17.9 g (0.10 mol) of the alcohol **6**[5] or **7**[6] is warmed to 80 °C and then 114 g (0.40 mol) of phosphorus tribromide is added dropwise. After complete addition the mixture is kept at 120 °C for 6 h. After cooling, hydrolizing by careful addition of ice-chips, and extraction with chloroform the organic layer is washed with water and sat. sodium hydrogen carbonate solution and dried over magnesium sulfate. Evaporation and recrystallization leads to 38 g (80%) of **8** or **9**.

**8**: M. p. 92 °C (CHCl$_3$). − $^1$H-NMR (60 MHz, CDCl$_3$, TMS): δ = 3.75 (d, 8 H); 2.85 (br. m, 4 H). C$_8$H$_{12}$Br$_4$   Calc. C 22.46 H 2.83 Br 74.71   Found C 22.58 H 2.95 Br 74.79

**9**: M. p. 59 − 60 °C (Lit.[7] 61 − 63 °C).

*cis,trans,cis- and trans,trans,trans-1,2,3,4-Cyclobutanetetraacetic acid* (**12** *and* **13**) *via the corresponding nitriles* **10** *and* **11**: 42.8 g (0.10 mol) of bromide **8** or **9**, 150 ml of water, 1.0 g of sodium iodide, and 150 g of potassium cyanide are refluxed in 500 ml of ethanol under nitrogen for 48 h. After filtering off the inorganic salts, the residual liquid is evaporated. The remaining

brown oil (**10** or **11**) is refluxed with 500 ml of conc. hydrochloric acid for 5 h. The precipitate is filtered after cooling, recrystallized, and dried: 20 g (70%) of light brown crystals.

**12**: M. p. 279 °C (decomp., from water). − [1] H NMR (90 MHz, [D$_6$]DMSO, ext. TMS): δ = 2.50 (br s, 12H); 11.8 (br, 4H).

$$C_{12}H_{16}O_6 \quad \text{Calc. C 50.00 H 5.60} \quad \text{Found C 49.78 H 5.79}$$

**13**: M. p. 311 − 313 °C (from water) [21].

*Tetramethyl cis,trans,cis- and trans,trans,trans-1,2,3,4-cyclobutanetetraacetate* (**14** and **15**): 20 g (70 mmol) of **12** or **13** are refluxed in 200 ml of absol. methanol saturated with HCl gas. Evaporation of the solvent is followed by washing of the residue with water. White crystals, 15 g (62%) yield.

**14**: M. p. 43 − 44 °C from ether. − ^{1}H NMR (60 MHz, CDCl$_3$, TMS): δ = 2.50 (br. s, 12H); 3.65 (s, 12H).    $C_{16}H_{24}O_8$ \quad Calc. C 55.80 H 7.03 \quad Found C 55.58 H 7.02

**15**: M. p. 63 − 64 °C (Lit. [22] 59 − 61 °C). − ^{1}H NMR (60 MHz, CDCl$_3$, TMS): = 2.00 (br. s, 4H); 2.50 (s, 8H); 3.64 (s, 12H).

*cis,trans,cis-1,2,3,4- and trans,trans,trans-1,2,3,4-Cyclobutanetetraethanol* (**16** and **17**): 10 g (29 mmol) of **14** or **15** in 100 ml of absol. tetrahydrofuran (THF) are added to a boiling suspension of 5.0 g of lithium aluminium hydride in 400 ml of absol. THF under nitrogen. After addition the mixture is refluxed for 3 h. Subsequent hydrolysis with a solution of 4.5 ml of water in 15 ml THF, 4.5 ml of 15% aq. sodium hydroxide, and 13.5 ml of water yields a precipitate which is filtered and extracted twice with THF and boiling methanol. The organic solvents are filtered through 200 g of cation exchange resin (H$^+$ form). After evaporation of the solvent and recrystallization from methanol 5.2 g (11.6 mmol, 77%) of **16** or **17** is obtained as colorless crystals.

**16**: M. p. 112 °C (methanol). − ^{1}H-NMR (60 MHz, CD$_3$OD, TMS): δ = 1.1 (m, 8H, CH); 1.45 (br. d, 4H, CH$_2$); 2.90 (t, 8H, CH$_2$OH); 4.25 (s, 4H, OH).

$$C_{12}H_{24}O_4 \quad \text{Calc. C 62.04 H 10.41} \quad \text{Found C 61.87 H 10.42}$$

**17**: M. p. 147 − 148 °C (methanol) [7].

*cis,trans,cis-1,2,3,4- and trans,trans,trans-1,2,3,4-Tetrakis(2-bromoethyl)cyclobutane* (**18** and **19**): The procedure used was identical to that used for the preparation of **8** and **9**. Yield for **18** and **19**: 70 − 80%.

**18**: M. p. 76 °C (methanol). − ^{1}H-NMR (60 MHz, CDCl$_3$, TMS): δ = 1.7 − 2.15 (m, 8H); 2.15 − 2.4 (br, d, 4H); 3.15 − 3.6 (m, 8H).

$$C_{12}H_{20}Br_4 \quad \text{Calc. C 29.78 H 4.17 Br 66.05} \quad \text{Found C 30.06 H 4.08 Br 65.84}$$

**19**: M. p. 39 − 40 °C (hexane) (Lit. [7] 37 − 38 °C). − ^{1}H-NMR (60 MHz, CDCl$_3$, TMS): δ = 1.70 (m, 4H); 1.98 (8H); 3.40 (8H, CH$_2$Br).

*cis,trans,cis- and trans,trans,trans-1,2,3,4-Tetraethenylcyclobutane* (**1** and **2**): To a boiling solution of 11.2 g (0.10 mol) of freshly sublimed potassium *tert*-butoxide in 100 ml of oxygen-free THF, 1.9 g (3.9 mmol) of the bromide **18** or **19** in 20 ml of absol. THF is quickly added under argon. The mixture is refluxed for 2 h. After cooling 30 ml of pure *n*-pentane and 9 ml of conc. hydrochloric acid in 20 ml of water are added, the inorganic salts are removed, and the organic layer is separated. To remove residual THF the organic layer is washed 10 times with 20 ml of water. The yellow pentane solution is filtered through a short aluminium oxide column (5 cm, 3 cm diameter, Woelm act. 1, basic) and eluated with pure pentane. Most of the solvent is removed by distillation. The crude product (ca. 600 ml) is distilled (15 Torr, 100 °C) in a bults tube distillation appa-

ratus (Büchi, Switzerland) or purified by preparative gas chromatography. It yields 424 mg (69%) of colorless liquid.

**1**: NMR (see Table 3 and 4). − MS (70 eV): $m/e$ = 160 (0.3%, M$^+$), 117 (1.5), 115 (1.1), 106 (1.9), 91 (9.2), 80 (92), 79 (100).

$$C_{12}H_{16} \quad \text{Calc. C 89.94 H 10.06} \quad \text{Found C 89.67 H 10.23}$$

**2**: NMR (see Table 3 and 4). − MS (70 eV): $m/e$ = 160 (0.5%, M$^+$), 124 (4), 110 (4), 91 (9.0), 80 (100), 79 (40).

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