difference map. The final four least-squares cycles included, in block-diagonal matrices (1 atom/block) coordinates and anisotropic thermal parameters for the nine heavy atoms, coordinates and isotropic temperature factors for the eight hydrogen atoms and a scale factor. The quantity minimized was $\Sigma w\ (|F_{obs}| - |F_{calc}|)^2$, with weights $w = (F_{obs}/0.85)^2$ for $F_{obs} < 0.85$, $w = (3.9/F_{obs})^2$ for $F_{obs} > 3.9$ and $w = 1$ for $0.85 < F_{obs} < 3.9$. The 440 unobserved reflections were given zero weight.

The final $R$ index is 0.048 for the 1754 observed reflections and 0.066 for all 2194 reflections with $2\,\Theta \leq 65°$[6]). Final coordinates and thermal parameters are listed in Table 4. Observed and calculated structure factors may be obtained in tabular form from one of the authors (G.R.).

All calculations were performed at our local computing center on an IBM/370–155 computer using our own program system.

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[6])    Estimated values of $F_{obs}$ for the unobserved reflections were computed from counting statistics by the data-reduction routine.

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# 286. Chemistry of Succinylsuccinic Acid Derivatives. Part III[1])

## The Crystal and Molecular Structure of
### *anti*-Tricyclo[4.4.0^{1,6}.0^{7,12}]-1,4,7,10-tetraethoxycarbonyl-3,6,9,12-tetrahydroxy-dodeca-3,9-diene, C24H32O12, a Photodimer of Diethyl Succinylsuccinate

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(5. X. 73)

*Summary.* X-ray structure analysis of the title compound (II) is reported. Diffractometer data and the Faltmolekül method were used. Refinement converged at R 0.044. The molecule assumes the *syn,syn*-conformation in the crystal.

Diethyl Succinylsuccinate (I) undergoes photodimerisation in the solid state [1]. From its packing geometry, found by X-ray crystal structure analysis [2], the formation of *anti*-tricyclo[4.4.0^{1,6}.0^{7,12}]-1,4,7,10-tetraethoxycarbonyl-3,6,9,12-tetrahydro-

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[1])    Part I. J. Sinnreich & H. Batzer [1]; Part. II. H.-C. Mez & G. Rihs [2].

xy-dodeca-3,9-diene (II) (ATCTETHDD) by a head-to-tail reaction was predicted. In order to test this conclusion, the present structure analysis of the photoproduct was carried out. Comparison between the structures of educt I and product II promised an insight into the geometric reaction coordinate of the topochemically controlled photodimerization.

*Scheme I*



(I)                                                        (II)
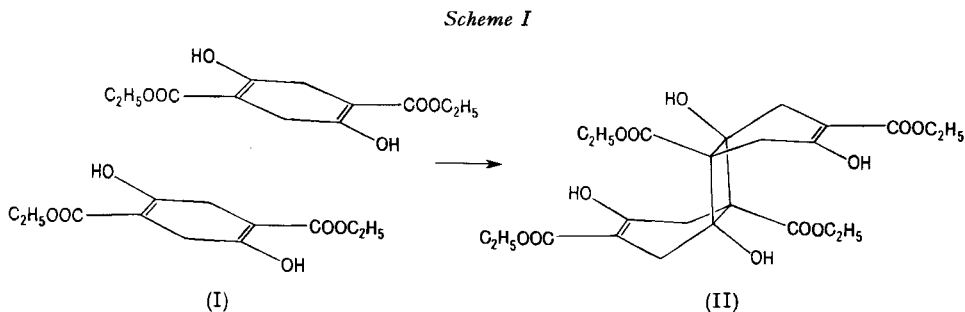
**Results**[2]). – The atomic numbering scheme, bond distances and angles in one half of the molecule are shown in Figure 1. The numbering scheme was chosen for reasons of clarity and differs somewhat from that used in Part I [1]. Estimated standard deviations, derived from the least-squares refinement, are 0.004 to 0.005 Å for distances between heavy atoms and 0.03 to 0.04 Å for distances between a heavy atom and a hydrogen atom. For more realistic values, 0.003 Å should be added to these values to account for uncertainties in cell parameters, atomic form factors, etc. Bond angles and their standard deviations are listed in Table 3 and torsion angles in Table 4.

A comparison of the molecular geometry with that of the monomer shows only small changes of the order of 0.01 Å and 1° in bond lengths and angles for the 'unreacted' moiety $O(3)$–$C(3)$–$C(4)$–$C(41)$-etc., as well as for the side chain $C(11)$–$O(12)$–$C(12)$–$C(13)$. All bonds and angles involving $C(1)$ and $C(6)$ are of course drastically changed. The cyclobutane ring is rectangular planar with bond lengths $C(1)$–$C(6)$ 1.573 Å and $C(1)$–$C(6')$ 1.593 Å. These may be compared to values in a table of simple cyclobutane compounds recently published by *Shirrell & Williams* [3]. The longest C–C bond of a precision comparable to the present analysis is $1.572 \pm 0.005$ Å, found in *cis,trans,cis*-1,2,3,4-tetramethoxycarbonylcyclobutane [4], a much less crowded molecule than II. An explanation of long C–C bonds in cyclobutanes in terms of non-bonded carbon-carbon repulsions was given by *Dunitz & Schomaker* [5].

The dimerization strongly influences the geometry of the intramolecular hydrogen bridge $O(6)$–$H(06)..O(11)$. The distance $C(11)$–$O(11)$, 1.203 Å, is significantly shorter than $C(41)$–$O(41)$, 1.223 Å, due to the lack of conjugation, and the bonds $C(11)$–$O(11)$ and $C(6)$–$O(6)$ are not coplanar, in contrast to $C(41)$–$O(41)$ and $C(3)$–$O(3)$. The result is an increase in the distance $O(11)..O(6)$ to 2.706 Å, *versus* 2.614 Å for $O(41)..O(3)$, and a concurrent weakening of the intramolecular hydrogen bond that manifests itself in the IR. spectrum [1].

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[2]) Crystallographic details and discussion of the solution of the crystal structure are contained in the Experimental section.
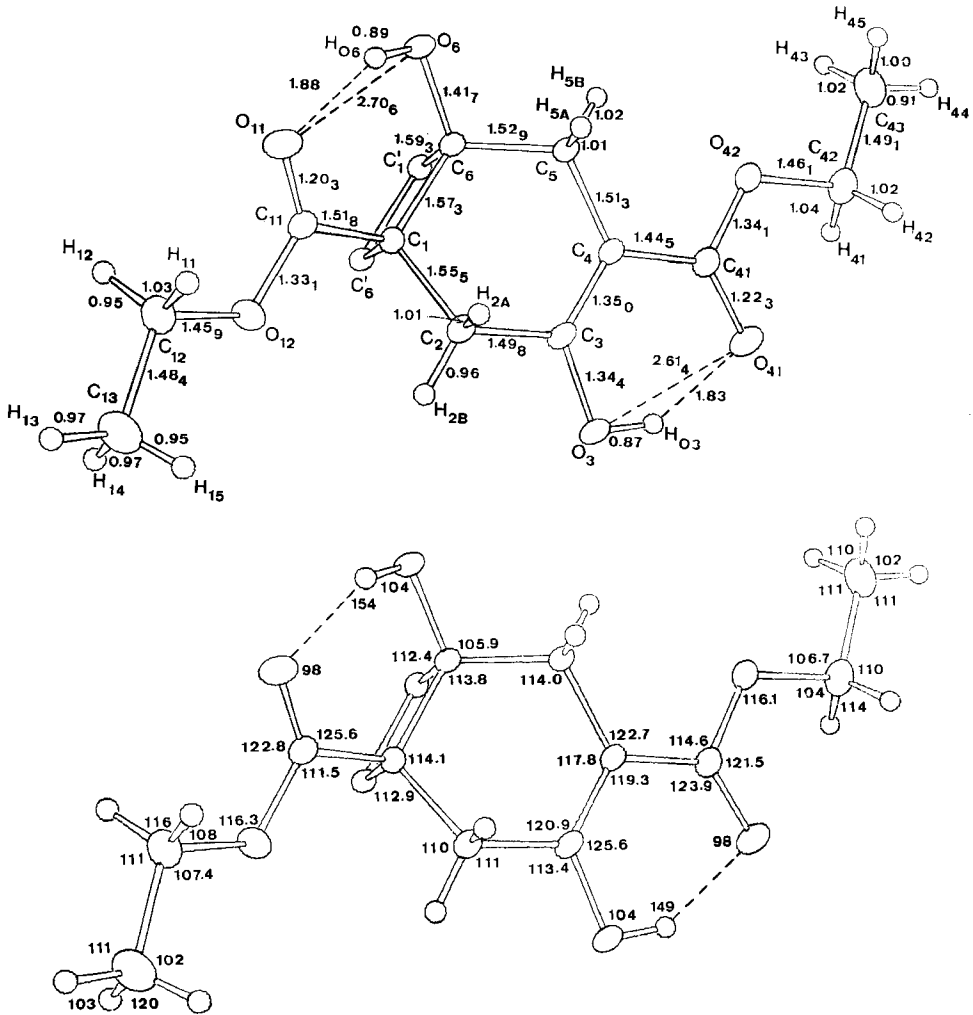
Fig. 1. *ATCTETHDD*

Atomic numbering scheme, bond lengths (Å) and angles (°) in the asymmetric half of one molecule[3]).
For a complete list of angles see Table 3

Figure 2 shows a stereo view[3]) of one molecule of II. Evidently, it is the head-to-tail dimer of I in the *syn, syn*-conformation predicted [2] from the crystal structure of the monomer. The planarity of the cyclobutane ring is a consequence of crystallographic symmetry. According to the general rule for predicting the conformation of cyclobutane compounds in the solid state [7], planar rings occur exclusively in centrosymmetrically substituted cyclobutanes. The cyclohexene rings assume slightly twisted boat shapes with an approximate mirror plane bisecting the bonds C(1)–C(6)

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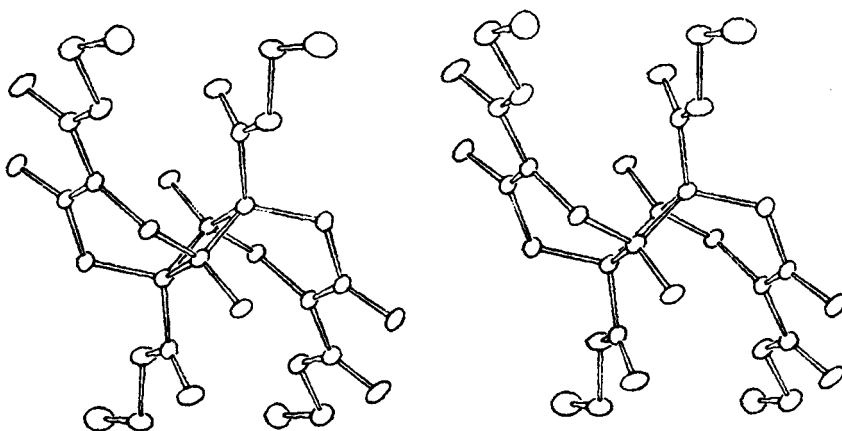
Fig. 2. *ATCTETHDD*
Stereo plot[3]) of one molecule

and C(3)–C(4). The overall conformation of the tricyclododecadiene skeleton may be characterized by the dihedral angle between the four-membered ring and the adjacent part of the six-membered ring, 117°, and that between the two halves of the six-membered ring, 142°.



Fig. 3. *ATCTETHDD*
Projection of a unit cell on the (010) plane along the b*) axis[3]). The four molecules shown are centered at (1,0,0), (0,0,0), (1,0,1) and (0,0,1)

The distortion of the six-membered ring from mirror plane symmetry is surprisingly large. It is presumably due to non-bonded interactions. Thus, repulsion between H(2B) and the lone pair electrons of O(12) across a non-bonded distance of 2.53 Å may 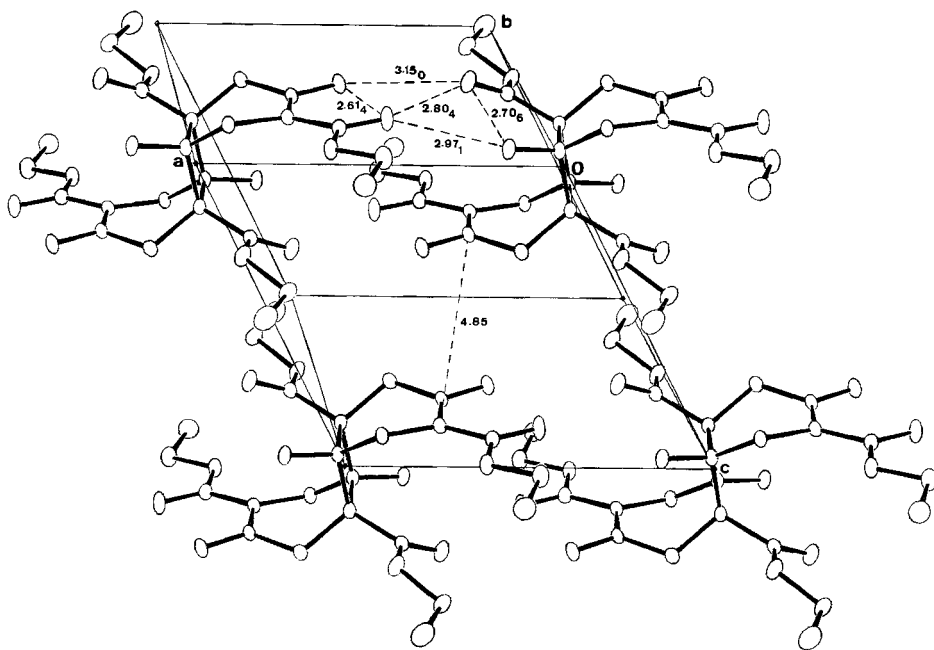contribute to the lengthening of C(1)–C(2), 1.555 Å, in comparison to C(5)–C(6), 1.529 Å. By the same argument, the non-bonded distance H(5B)..O(42) of 2.43 Å length may contribute to the lengthening of C(4)–C(5), 1.513 Å, compared to C(2)–C(3), 1.498 Å.

Figure 3 illustrates the packing of molecules within the crystal structure. The similarity of the (001) plane in II to the (010) plane in I is rather striking. The inter-molecular hydrogen bonds O(6)–H(06)..O(41'), 2.97 Å long, and O(3)–H(03)..O(11''), 3.15 Å long, correspond to the symmetry-related pair of length 2.96 Å in I, and result in an O(11)..O(41') approach of 2.80 Å, with a corresponding value 2.78 Å in I.

**Discussion.** – The photodimerization of I has been shown to yield the predicted product II. One of the initial objectives in determining the crystal structures of both educt and product was to provide 'before' and 'after' models for the photodimerization. In Figure 4 we present a superposition of two molecules of educt I, drawn in thin lines, as found in the crystal structure analysis [2] and one molecule of product, in fat lines, from the present analysis.

The 'topochemical postulate' of *Cohen & Schmidt* [8] that reaction in the solid state occurs with a minimum of atomic or molecular movement is beautifully illustrated. Only C(1) and C(6) move by more than 1 Å, pulling the hydroxyl group O(6) and
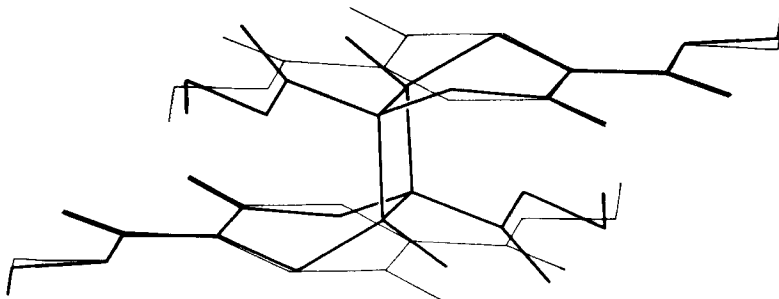


Fig. 4. *ATCTETHDD*

Superposition of two molecules of educt I, thin lines, as found in the crystal [2], and one molecule of photodimer II, fat lines, as found in the present analysis.

the ethoxycarbonyl side chain C(11)-etc. along. The 'unreacted' part of the monomer molecule is barely affected by the dimerization.

A second objective in determining the present crystal structures was to obtain information on the possibility of other topochemical reactions in crystalline I apart from photodimerization. We find that dimers are not likely to react with neighbouring molecules to yield trimers or higher oligomers because the double bond C(3)–C(4) in the dimer is presumably immobilized by the formation of the tricyclododecadiene system. The six-membered ring at the center of a trimer being roughly similar to the six-membered ring in the dimer, the third molecule would have to move by more than 2 Å in a geometrically awkward fashion. The crystal lattice leaves no room for

this type of reaction. This finding is supported by the experimental evidence that the photoreaction product is nearly pure II. A small peak obtained in the TLC may be due to traces of trimer, but was too small to allow isolation of the substance [9].

For the dimer in the present crystal structure, geometric considerations appear to rule out the possibility of further photodimerization in the solid state at room temperature. The distance between double bonds in adjacent molecules is 4.85 Å.

## Experimental

*Data collection.* Colourless crystals of II, obtained by recrystallization from toluene at 100°, were provided by Dr *J. Sinnreich*. A suitable crystal of dimensions $0.26 \times 0.20 \times 0.03$ mm$^3$ was glued to the tip of a *Lindemann* glass capillary tube. After preliminary rotation, *Weissenberg* and precission photographs it was transferred to a *Picker*-FACS-I automatic diffractometer. Cell dimensions were obtained from a least-squares fit to setting angles $(2\,\Theta, \chi, \varphi)$ for 12 reflections; they are given in Table 1.

Table 1. *Crystal Data*

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*anti*-Tricyclo[4.4.0$^{1,6}$.0$^{7,12}$]-1,4,7,10-tetraethoxycarbonyl-3,6,9,12-tetrahydroxy-dodeca-3,9-diene,    $C_{24}H_{32}O_{12}$

Triclinic    F.W. = 512.52

Space group $P_{\bar{1}}$ (from $E$-value statistics [10])

$a = 8.869$ (6), $b = 10.189$ (6), $c = 8.146$ (6) Å$^a$),

$\alpha = 115.1$ (5)°, $\beta = 116.6$ (5)°, $\gamma = 80.5$ (5)°,

$V = 596.2$ (12) Å$^3$, $Z = 1$, $D_x = 1.43$ g · cm$^{-3}$

$\mu = 1.37$ cm$^{-1}$, $\lambda$ (Mo$K\alpha$) = 0.71069 Å

Molecular symmetry $C_i$

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[a]) Standard deviations of the least significant figures, given in parentheses, are three times the values obtained from the least-squares calculation.

Intensities were measured using Mo$K\alpha$ radiation with a graphite monochromator and $\Theta - 2\,\Theta$ step scans with a step width of 0.04° (2 $\Theta$); the time spent on each step was 2 s, with 40 s spent at the extrema for background counting[4]). Three reference reflections (200, 050, 0$\bar{3}$3) were monitored every 30 reflections; their intensities fluctuated by about $\pm 6\%$ in the course of the data collection[5]). All reflections in one half of reciprocal space ($l \geq 0$) out to $2\,\Theta = 46°$ were surveyed; they numbered 1645, of which 1410 with I $= 2\,\sigma$ (I) were accepted as observed. Observational variances $\sigma^2$ (I) were based on counting statistics plus an additional term $(0.03S)^2$, where $S$ is the scan count. Intensities and their standard deviations were corrected for the fluctuations of the reference reflection intensities and for *Lorentz* and polarization factors, and reduced to structure amplitudes, $F_{obs}$. No absorption correction was applied ($\mu_{max} \sim 0.05$).

*Structure determination and refinement.* $E$-value statistics [10] confirmed the presence of the predicted center of symmetry ($\langle E \rangle = 0.776$, $\langle E^2 - 1 \rangle = 1.047$, $\langle E^2 \rangle = 1.000$). Attempts to determine the structure by direct methods, notoriously difficult in triclinic crystals, were unsuccessful. We therefore decided to apply a local version of the «Faltmolekül» (molecular convolution) program of *Huber* [11]. Three models were tested as input. The first one consisted of the twelve heavy atoms in boatshaped 1-ethoxycarbonyl-2-hydroxy-cyclohexene, derived from the coordinates of I[6]). The overlap function of its self-convolution with the *Patterson* synthesis showed

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[4]) The Vanderbilt University Disk Oriented Program System was used to control the diffractometer. It is a pleasure to thank Prof *P. G. Lenhert* for a copy of his programs.

[5]) The instability resulted from electronic failure in the counting chain of the diffractometer. For the purposes of the present analysis, we considered the accuracy of the measurements entirely sufficient.

[6]) Orthonormalized parameters for our models were calculated with the help of 'MODL', a FOCAL program, on a DEC PDP-8/I computer.

Table 2a. *ATCTETHDD: Fractional atomic coordinates and their estimated standard deviations*[a])

| Atom | $x/a$ | | $y/b$ | | $z/c$ | |
|------|-------|------|-------|------|-------|------|
| O(3) | 0.49516 | (23) | − 0.05432 | (22) | 0.24247 | (31) |
| O(6) | − 0.12886 | (24) | 0.19205 | (21) | 0.15455 | (31) |
| O(11) | − 0.14733 | (28) | − 0.01376 | (23) | 0.27303 | (35) |
| O(12) | − 0.02386 | (26) | − 0.22417 | (21) | 0.18191 | (32) |
| O(41) | 0.58510 | (25) | 0.17772 | (24) | 0.24308 | (36) |
| O(42) | 0.40500 | (23) | 0.35906 | (21) | 0.23494 | (31) |
| C(1) | 0.04380 | (34) | − 0.03888 | (30) | 0.12296 | (43) |
| C(2) | 0.23176 | (35) | − 0.05782 | (32) | 0.25151 | (44) |
| C(3) | 0.35347 | (34) | 0.01863 | (32) | 0.23773 | (42) |
| C(4) | 0.32083 | (33) | 0.15089 | (30) | 0.23106 | (43) |
| C(5) | 0.15819 | (33) | 0.21931 | (30) | 0.23932 | (43) |
| C(6) | 0.00559 | (34) | 0.11397 | (30) | 0.11102 | (43) |
| C(11) | − 0.05626 | (35) | − 0.08808 | (31) | 0.19803 | (44) |
| C(12) | − 0.10111 | (41) | − 0.27877 | (35) | 0.26661 | (50) |
| C(13) | − 0.02240 | (51) | − 0.41834 | (39) | 0.27044 | (61) |
| C(41) | 0.44769 | (36) | 0.22668 | (32) | 0.23553 | (44) |
| C(42) | 0.53409 | (41) | 0.44235 | (37) | 0.25152 | (55) |
| C(43) | 0.45655 | (46) | 0.58082 | (37) | 0.23737 | (56) |
| H(03) | 0.5586 | (38) | 0.0049 | (33) | 0.2472 | (45) |
| H(06) | − 0.1533 | (38) | 0.1458 | (32) | 0.2107 | (45) |
| H(2 A) | 0.2528 | (37) | − 0.0111 | (32) | 0.3975 | (45) |
| H(2 B) | 0.2556 | (38) | − 0.1594 | (32) | 0.2180 | (45) |
| H(5 A) | 0.1703 | (38) | 0.2638 | (32) | 0.3811 | (45) |
| H(5 B) | 0.1306 | (38) | 0.3012 | (32) | 0.1898 | (45) |
| H(11) | − 0.0773 | (39) | − 0.2031 | (33) | 0.4083 | (46) |
| H(12) | − 0.2163 | (38) | − 0.2935 | (32) | 0.1732 | (45) |
| H(13) | − 0.0754 | (39) | − 0.4626 | (33) | 0.3169 | (46) |
| H(14) | − 0.0435 | (38) | − 0.4898 | (33) | 0.1371 | (45) |
| H(15) | 0.0906 | (38) | − 0.3878 | (32) | 0.3666 | (45) |
| H(41) | 0.5652 | (39) | 0.3752 | (32) | 0.1338 | (46) |
| H(42) | 0.6312 | (39) | 0.4626 | (33) | 0.3889 | (46) |
| H(43) | 0.3607 | (39) | 0.5614 | (33) | 0.0998 | (46) |
| H(44) | 0.5329 | (39) | 0.6409 | (33) | 0.2556 | (45) |
| H(45) | 0.4164 | (39) | 0.6434 | (32) | 0.3429 | (45) |

[a])   Standard deviations of the least significant figures, given in parentheses, are values obtained from the least-squares calculation. They represent a lower value of the uncertainties.

maxima every 60° in psi and was useless. The second and third models were, respectively, the *syn, syn-* and the *anti, anti-*conformers of *anti-*tricyclo[4.4.0$^{1,6}$,0$^{7,12}$]-1, 4, 7, 10-tetramethyl-3, 6, 9, 12-tetrahydroxy-dodeca-3, 9-diene (III, IV). From the crystal structure of the monomer [2], formation of the *syn, syn-*conformer had been predicted, but a change of conformation on recrystallization from a solution at 100° could not be ruled out a priori. A comparison of the overlap functions for the self-convolutions of the two models III and IV established the correctness of the *syn, syn-*model.

*Euler* parameters were interpolated from a series of rotation maps calculated with a 5° grid for the three *Euler* angles. Positional and isotropic thermal parameters for the ten atoms in the asymmetric unit obtained from model III were refined by one cycle of block-diagonal least-

Table 2b. *ATCTETHDD*: *Thermal parameters*

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{23}$ | $b_{31}$ |
|------|------|------|------|------|------|------|
| O(3) | 0.00794 | 0.01159 | 0.03005 | 0.00559 | 0.02022 | 0.01536 |
| O(6) | 0.01104 | 0.00950 | 0.02962 | 0.00744 | 0.01723 | 0.02599 |
| O(11) | 0.01747 | 0.01284 | 0.03932 | 0.01284 | 0.02788 | 0.03982 |
| O(12) | 0.01816 | 0.00883 | 0.03115 | 0.00498 | 0.01890 | 0.03271 |
| O(41) | 0.01049 | 0.01545 | 0.04413 | 0.00603 | 0.02821 | 0.02948 |
| O(42) | 0.01009 | 0.01008 | 0.02983 | − 0.00071 | 0.01749 | 0.01788 |
| C(1) | 0.00853 | 0.00797 | 0.01959 | 0.00146 | 0.01303 | 0.01303 |
| C(2) | 0.00847 | 0.00980 | 0.02162 | 0.00181 | 0.01677 | 0.01005 |
| C(3) | 0.00668 | 0.01056 | 0.01767 | 0.00250 | 0.01253 | 0.00876 |
| C(4) | 0.00758 | 0.00846 | 0.01736 | 0.00038 | 0.01048 | 0.00926 |
| C(5) | 0.00777 | 0.00768 | 0.01988 | 0.00130 | 0.00974 | 0.01262 |
| C(6) | 0.00824 | 0.00747 | 0.02075 | 0.00305 | 0.01173 | 0.01538 |
| C(11) | 0.00874 | 0.00946 | 0.01951 | 0.00162 | 0.01413 | 0.01090 |
| C(12) | 0.01823 | 0.01176 | 0.02935 | 0.00136 | 0.02281 | 0.02679 |
| C(13) | 0.02897 | 0.01429 | 0.04397 | 0.00637 | 0.03231 | 0.04102 |
| C(41) | 0.00961 | 0.01028 | 0.01985 | − 0.00116 | 0.01204 | 0.01211 |
| C(42) | 0.01378 | 0.01421 | 0.03635 | − 0.00455 | 0.02383 | 0.01964 |
| C(43) | 0.02147 | 0.01272 | 0.03200 | − 0.00721 | 0.01950 | 0.01779 |

The anisotropic temperature factor is defined by

$$B = \exp - [h^2 \cdot b_{11} + k^2 \cdot b_{22} + l^2 \cdot b_{33} + h \cdot k \cdot b_{12} + k \cdot l \cdot b_{23} + l \cdot h \cdot b_{31}]$$

*Scheme II*



(III)　　　　　　　　　　　　　(IV)

*syn, syn-*　　　　　　　　　　*anti, anti-*
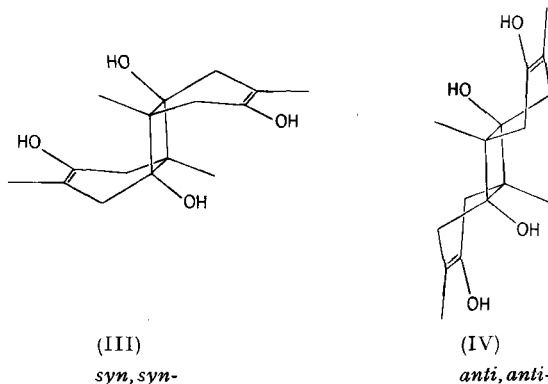
*anti*-tricyclo[4.4.0$^{1,6}$.0$^{7,12}$]-1, 4, 7, 10-tetramethyl-3, 6, 9, 12-tetrahydroxy-dodeca-3, 9-diene

squares (1 atom/block), and a subsequent beta-synthesis [12] with *Sim* weights [13] and cutoff [14] revealed the positions of all eighteen non-hydrogen atoms. Block-diagonal least-squares refinement of the coordinates and thermal parameters, first isotropic, then anisotropic, led to an $R$ ($= \Sigma_{\|} |F_{\rm obs}| - |F_{\rm calc}| |/\Sigma |F_{\rm obs}|$) index of 0.095 for the 1410 observed reflections. Positions of the sixteen hydrogen atoms were taken from a three-dimensional difference map and included in the block-diagonal least-squares refinement; the thermal parameters for the hydrogen atoms were fixed at $B = 3.5$ Å$^2$. After the shifts of the hydrogen atoms had settled down, two final cycles of full-matrix least-squares refinement were calculated with coordinates and anisotropic

Table 3. *ATCTETHDD: Angles(°) and their estimated standard deviations* [a]

| | | | | | |
|---|---|---|---|---|---|
| C(3) | —O(3)—H(03) | 104.2 (22) | O(6) | —C(6)—C(1) | 118.4 (3) |
| C(6) | —O(6)—H(06) | 104.1 (22) | O(6) | —C(5) | 105.9 (3) |
| O(3) | —H(03)—O(41) | 149.1 (32) | O(6) | —C(1') | 112.4 (3) |
| O(6) | —H(06)—O(11) | 153.7 (32) | C(1) | —C(5) | 113.8 (3) |
| C(11) | —O(11)—H(06) | 98.0 (22) | C(1) | —C(1') | 89.8 (2) |
| C(11) | —O(12)—C(12) | 116.3 (3) | C(5) | —C(1') | 116.6 (3) |
| C(41) | —O(41)—H(03) | 97.7 (11) | O(11) | —C(11)—O(12) | 122.8 (3) |
| C(41) | —O(42)—C(42) | 116.1 (3) | O(11) | —C(1) | 125.6 (3) |
| C(2) | —C(1)—C(6) | 114.1 (3) | O(12) | —C(1) | 111.5 (3) |
| C(2) | —C(11) | 105.2 (3) | O(12) | —C(12)—C(13) | 107.4 (3) |
| C(2) | —C(6') | 112.9 (3) | O(12) | —H(11) | 107.6 (19) |
| C(6) | —C(11) | 117.7 (3) | O(12) | —H(12) | 103.1 (22) |
| C(6) | —C(6') | 90.2 (2) | C(13) | —H(11) | 111.2 (20) |
| C(11) | —C(6') | 116.8 (3) | C(13) | —H(12) | 111.1 (20) |
| C(1) | —C(2)—C(3) | 113.7 (3) | H(11) | —H(12) | 115.8 (29) |
| C(1) | —H(2A) | 108.6 (19) | C(12) | —C(13)—H(13) | 110.5 (20) |
| C(1) | —H(2B) | 110.2 (21) | C(12) | —H(14) | 111.5 (21) |
| C(3) | —H(2A) | 104.8 (19) | C(12) | —H(15) | 101.9 (20) |
| C(3) | —H(2B) | 111.1 (20) | H(13) | —H(14) | 103.0 (29) |
| H(2A) | —H(2B) | 108.2 (29) | H(13) | —H(15) | 110.2 (31) |
| O(3) | —C(3)—C(2) | 113.4 (3) | H(14) | —H(15) | 119.7 (30) |
| O(3) | —C(4) | 125.6 (3) | O(41) | —C(41)—O(42) | 121.5 (3) |
| C(2) | —C(4) | 120.9 (3) | O(41) | —C(4) | 123.9 (3) |
| C(3) | —C(4)—C(5) | 117.8 (3) | O(42) | —C(4) | 114.6 (3) |
| C(3) | —C(41) | 119.3 (3) | O(42) | —C(42)—C(43) | 106.7 (3) |
| C(5) | —C(41) | 122.7 (3) | O(42) | —H(41) | 104.2 (19) |
| C(4) | —C(5)—C(6) | 114.0 (3) | O(42) | —H(42) | 106.9 (20) |
| C(4) | —H(5A) | 110.4 (20) | C(43) | —H(41) | 114.5 (19) |
| C(4) | —H(5B) | 109.8 (19) | C(43) | —H(42) | 110.2 (19) |
| C(6) | —H(5A) | 108.3 (20) | H(41) | —H(42) | 113.6 (28) |
| C(6) | —H(5B) | 107.0 (20) | C(42) | —C(43)—H(43) | 110.5 (19) |
| H(5A) | —H(5B) | 107.1 (27) | C(42) | —H(44) | 111.2 (22) |
| | | | C(42) | —H(45) | 116.0 (20) |
| | | | H(43) | —H(44) | 107.1 (30) |
| | | | H(43) | —H(45) | 109.5 (29) |
| | | | H(44) | —H(45) | 101.9 (30) |

[a]    Standard deviations of the least significant figures, given in parentheses, are derived from the e.s.d.'s of the positional parameters, neglecting errors in cell parameters, etc. For realistic values, about 0.3° should be added.

thermal parameters for just the eighteen heavy atoms and a scale factor, with the hydrogen atom contributions kept constant. The quantity minimized was $\Sigma\ w\ (|F_{obs}| - |F_{calc}|)^2$, with $w = 1/\sigma\ (F_{obs})$. The 235 unobserved reflections were given zero weight throughout the refinement. One reflection, (381), had apparently been measured incorrectly and was excluded.

The final $R$ index is 0.044 for the 1409 observed reflections, 0.056 for all 1645 reflections [7] and 0.038 for the 1275 most reliable ones with $F_{obs} \geq 2\ \sigma\ (F_{obs})$. Final coordinates and thermal

[7]    Estimated values of $F_{obs}$ for the unobserved reflections were computed from counting statistics by the data-reduction routine.

Table 4. *ATCTETHDD: Torsion angles*

| | | | | | |
|---|---|---|---|---|---|
| H(03) | —O(3)—3(3)—C(2) | 174° | C(2) | —C(1)—C(6')—C(1') | 116° |
| H(03) | —C(4) | − 3° | C(6) | —C(1') | 0° a) |
| H(06) | —O(6)—C(6)—C(1) | − 13° | C(11) | —C(1') | −121° |
| H(06) | —C(5) | 116° | O(3) | —C(3)—C(4)—C(5) | 176° |
| H(06) | —C(1') | −116° | O(3) | —C(41) | 2° |
| C(12) | —O(12)—C(11)—O(11) | 2° | C(2) | —C(5) | 0° |
| C(12) | —C(1) | −175° | C(2) | —C(41) | −175° |
| C(11) | —O(12)—C(12)—C(13) | 169° | C(3) | —C(4)—C(5)—C(6) | 42° |
| C(11) | —H(11) | 49° | C(3) | —H(5A) | − 80° |
| C(11) | —H(12) | − 74° | C(3) | —H(5B) | 162° |
| C(42) | —O(42)—C(41)—O(41) | 2° | C(41) | —C(6) | −144° |
| C(42) | —C(4) | −176° | C(41) | —H(5A) | 94° |
| C(41) | —O(42)—C(42)—C(43) | −177° | C(41) | —H(5B) | − 24° |
| C(41) | —H(41) | − 56° | C(3) | —C(4)—C(41)—O(41) | − 1° |
| C(41) | —H(42) | 65° | C(3) | —O(42) | 178° |
| C(6) | —C(1)—C(2)—C(3) | 35° | C(5) | —O(41) | −175° |
| C(6) | —H(2A) | − 81° | C(5) | —O(42) | 4° |
| C(6) | —H(2B) | 161° | C(4) | —C(5)—C(6)—O(6) | −174° |
| C(11) | —C(3) | 166° | C(4) | —C(1) | − 42° |
| C(11) | —H(2A) | 49° | C(4) | —C(1') | 61° |
| C(11) | —H(2B) | − 69° | H(5A) | —O(6) | − 50° |
| C(6') | —C(3) | − 66° | H(5A) | —C(1) | 81° |
| C(6') | —H(2A) | 178° | H(5A) | —C(1') | −176° |
| C(6') | —H(2B) | 59° | H(5B) | —O(6) | 65° |
| C(2) | —C(1)—C(6)—O(6) | 129° | H(5B) | —C(1) | −163° |
| C(2) | —C(5) | 4° | H(5B) | —C(1') | − 61° |
| C(2) | —C(1') | −115° | O(6) | —C(6)—C(1')—C(6') | 121° |
| C(11) | —O(6) | 5° | C(1) | —C(6') | 0° a) |
| C(11) | —C(5) | −120° | C(5) | —C(6') | −117° |
| C(11) | —C(1') | 121° | O(12) | —C(12)—C(13)—H(13) | 176° |
| C(6') | —O(6) | −115° | O(12) | —H(14) | 62° |
| C(6') | —C(5) | 119° | O(12) | —H(15) | − 67° |
| C(6') | —C(1') | 0° a) | H(11) | —H(13) | − 67° |
| C(2) | —C(1)—C(11)—O(11) | −118° | H(11) | —H(14) | 179° |
| C(2) | —O(12) | 68° | H(11) | —H(15) | 50° |
| C(6) | —O(11) | 10° | H(12) | —H(13) | 64° |
| C(6) | —O(12) | −174° | H(12) | —H(14) | − 50° |
| C(6') | —O(11) | 116° | H(12) | —H(15) | −179° |
| C(6') | —O(12) | − 68° | O(42) | —C(42)—C(43)—H(43) | 65° |
| C(1) | —C(2)—C(3)—O(3) | 144° | O(42) | —H(44) | −176° |
| C(1) | —C(4) | − 39° | O(42) | —H(45) | − 60° |
| H(2A) | —O(3) | − 98° | H(41) | —H(43) | − 50° |
| H(2A) | —C(4) | 79° | H(41) | —H(44) | 69° |
| H(2B) | —O(3) | 19° | H(41) | —H(45) | −175° |
| H(2B) | —C(4) | −164° | H(42) | —H(43) | −179° |
| | | | H(42) | —H(44) | − 60° |
| | | | H(42) | —H(45) | 55° |
| | | | C(6) | —C(1')—C(6')—C(1) | 0° a) |

a) Value of 0.0° fixed by symmetry.

parameters are listed in Tables 2a and 2b. Observed and calculated structure factors may be obtained in tabular form from one of the authors (G. R.).

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# 287. 3-Amino-3-desoxyverbindungen von Uzarigenin, Oleandrigenin, Gitoxigenin und Digoxigenin[1])

Partialsynthetische Versuche in der Reihe der Herzgifte, 6. Mitt.[2])

von **Emil Hauser, Ursula Boffo, Lotte Meister, Ludwika Sawlewicz, Horst H. A. Linde** und **Kuno Meyer**

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Herrn Prof. Dr. Emil Hardegger mit den besten Wünschen zum
60. Geburtstag gewidmet

(8. X. 73)

*Zusammenfassung.* Es werden die Partialsynthesen der 3-Aminoverbindungen der im Titel genannten Cardenolide beschrieben.

Kürzlich [2] berichteten wir über den Austausch der 3-ständigen HO-Gruppe in dem am leichtesten zugänglichen Cardenolid Digitoxigenin gegen die Amino-Gruppe,

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[1]    Diese Arbeiten sind schon vor mehreren Jahren im Rahmen eines grösseren Projektes ausgeführt worden [1].
[2]    5. Mitt. siehe [2].