285. Chemistry of Succinylsuccinic Acid Derivatives. Part II[1]) The Crystal and Molecular Structure of Diethyl Succinylsuccinate

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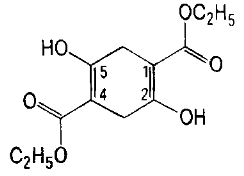
(5. X. 73)

Summary. X-ray structure analysis of the title compound (I) is reported. The results are interpreted to predict formation 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 on UV.-irradiation of solid (I).

Scheme 1



(I)

The solution chemistry of succinylsuccinic esters is well documented [2]. The solid state chemistry, on the other hand, has not formerly been investigated.

Crystal structure determinations for the two modifications of dimethyl succinylsuccinate (DMSS) have been reported by *Ganis et al.* [3] [4], and inspection of the molecular packing in the crystal with regard to possible topochemical reactions [5] suggested the possibility of photodimerization in the triclinic modification.

Recrystallization of the title compound (DESS, I) from different solvents yielded only triclinic crystals. In order to understand their susceptibility to topochemical reactions and to obtain precise geometric parameters for the DESS molecule, the present *X*-ray structure determination was performed. It promised, moreover, an insight into the structure of the eventual photoproducts.

Results.[2]). – a) *Molecular structure.* Figure 1 shows an isolated molecule of (I) with bond distances and angles[3]). Estimated standard deviations derived from the least-squares refinement are about 0.001 Å in the distances and 0.1° in the angles not involving hydrogen atoms, 0.02 Å in the distances and 1° in the angles involving one hydrogen atom, and 1.5° in angles involving two hydrogen atoms. For more realistic values, 0.003 Å or 0.3° should be added to these values to account for uncertainties in cell parameters, atomic form factors etc.. The molecular structure is similar to that of DMSS in both its modifications [3] [4]. The cyclohexa-1,4-diene ring is very nearly

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[1]) Part I. *J. Sinnreich & H. Batzer* [1].

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

[3]) Figure plotted by ORTEP [6]. It is a pleasure to thank Dr *C. K. Johnson* for a copy of the program.

C(1′)	—C(3)—H(3B)	112
C(2)	—C(3)—H(3A)	105
O(3)	—C(5)—H(5B)	108
C(6)	—C(5)—H(5A)	110
C(5)	—C(6)—H(6A)	112
H(6B)	—C(6)—H(6C)	111

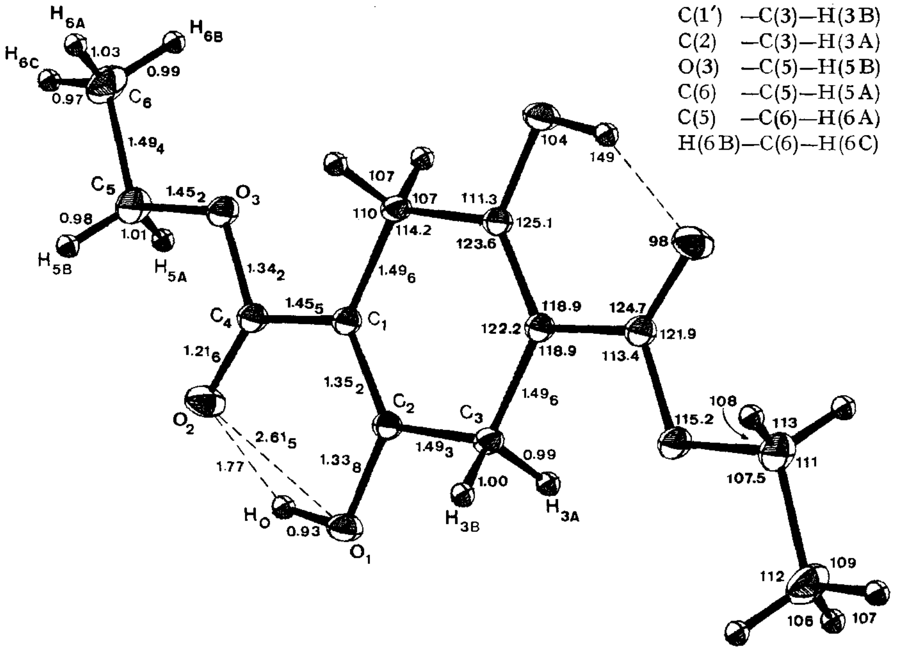

Fig. 1. *DESS*: *Bond lengths* (Å) *and angles* (°) *in a molecule*[3])

planar with alternating torsion angles of ±3°; the chair shape is an artefact resulting from the molecular symmetry, C_i, and we do not regard the deviation from planarity as significant. From strain energy calculations the planar conformation has been reported to be 2.8 kcal/mol^{-1} [7] more favourable than a boat one for the cyclohexa-1,4-diene molecule. The lengths of the double and single bonds, 1.352 and 1.494

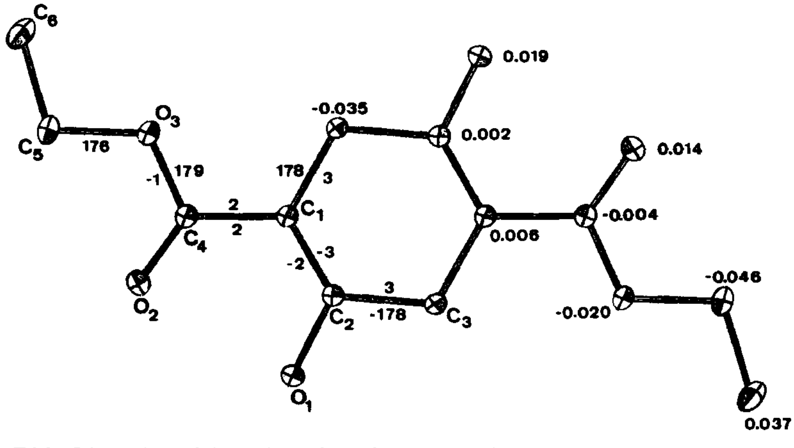

Fig. 2. *DESS*: ***Molecule with best plane through all non-hydrogen atoms parallel to drawing plane***[3]). Figures in right half represent distances (Å) of atoms from this plane, figures in left half are torsion angles (°)

(averaged) Å, agree reasonably with the averaged results for cyclohexa-1,4-diene-1-glycine, 1.347 and 1.485 Å [8].

The geometry and conformation of the side chains are governed by the intramolecular hydrogen bridge O(1)–H(0)..O(2) and antiperiplanar conformations around C(4)–O(3) and O(3)–C(5). The resulting planarity of the molecule is illustrated in Figure 2, which shows some relevant torsion angles and the distances from a best plane through all non-hydrogen atoms in a molecule. The equation of this plane in crystal coordinates is $3.1616\, x/a + 3.4853\, y/b - 0.1405\, z/c = 0$. A list of torsion angles is given in Table 1.

Table 1. *Diethyl Succinylsuccinate*: *Torsion Angles*

C(1) —C(2)—C(3)—C(1′)	3°	C(3′) —C(1)—C(4)—O(3)	2°
C(1) —H(3A)	−118°	C(3′) —O(2)	−178°
C(1) —H(3B)	127°	C(2) —O(3)	−179°
O(1) —C(1′)	−178°	C(2) —O(2)	2°
O(1) —H(3A)	61°	O(3) —C(4)—O(2)—H(O)	−179°
O(1) —H(3B)	− 53°	C(1) —H(O)	0°
C(3′) —C(1)—C(2)—C(3)	− 3°	C(1) —C(4)—O(3)—C(5)	179°
C(3′) —O(1)	178°	O(2) —C(5)	− 1°
C(4) —C(3)	178°	C(4) —O(3)—C(5)—C(6)	176°
C(4) —O(1)	− 2°	C(4) —H(5A)	− 65°
C(2) —C(3)—C(1′)—C(2′)	− 3°	C(4) —H(5B)	57°
C(2) —C(4′)	178°	O(3) —C(5)—C(6)—H(6A)	− 63°
H(3A)—C(2′)	116°	O(3) —H(6B)	56°
H(3A)—C(4′)	− 64°	O(3) —H(6C)	179°
H(3B)—C(2′)	−125°	H(5A)—H(6A)	180°
H(3B)—C(4′)	55°	H(5A)—H(6B)	− 61°
C(1) —C(2)—O(1)—H(O)	− 1°	H(5A)—H(6C)	62°
C(3) —H(O)	179°	H(5B)—H(6A)	54°
		H(5B)—H(6B)	173°
		H(5B)—H(6C)	− 64°

b) *Packing of molecules.* The molecular packing arrangement is quite similar to that of the triclinic modification of DMSS [3]. Figure 3 shows a projection of one layer of molecules on the (010) plane. The molecules are packed in parallel flat layers approximately perpendicular to (110). Within the layers, weak intermolecular hydrogen bonds run parallel to the *a*-axis, as evidenced by distances O(1)..O(2″) of length 2.96 Å and O(2)..O(2″) of length 2.78 Å; corresponding values for triclinic DMSS are 3.05 and 2.86 Å[4]). *Van der Waals* contacts govern the packing parallel to the *c*-axis, and an interplanar layer distance of 3.49 Å determines the packing along the *b*-axis.

Discussion. – The topochemical postulate, first formulated by *Cohen & Schmidt* [5], may be interpreted in terms of geometric prerequisites for the occurence of topochemical reactions. Table 2 is a compilation of distances and angles describing the mutual arrangement of double bonds in the crystal, and Figure 4 shows three mole-

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[4]) These values were calculated from the parameters in [3]; they are not the same as quoted in [3].

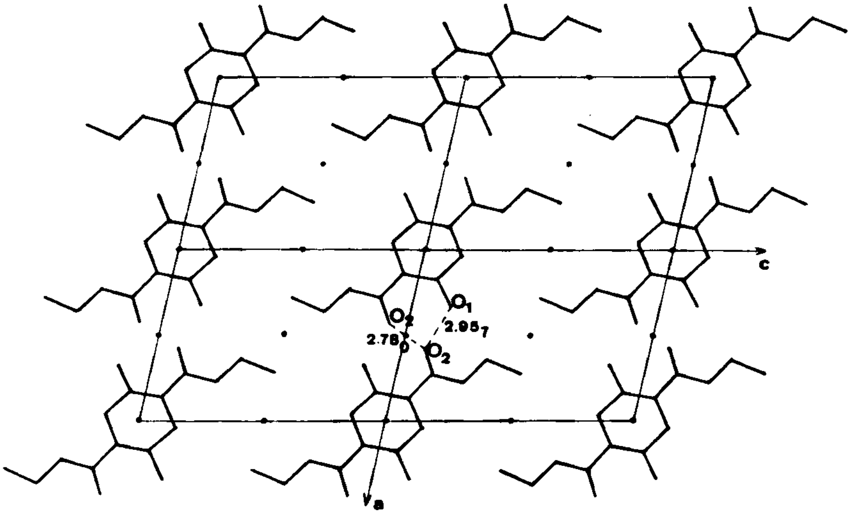

Fig. 3. *DESS: Projection of structure on the (010) plane*

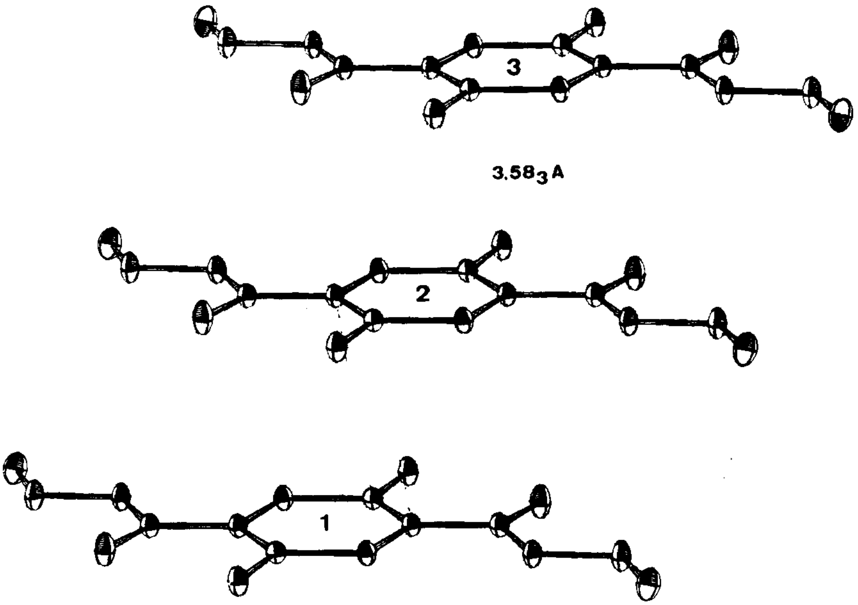

Fig. 4. *DESS: Three molecules related by the b-axis translation.* The drawing plane is inclined 60° around C(1) ... C(1′) to the best plane through all non-hydrogen atoms[3])

cules related by the *b*-axis translation. It is evident from the geometry that the observed photoreaction [1] has to be a head-to-tail dimerization leading to the formation 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 with the two six-membered rings *syn* to the four-membered ring. The confirmation of this conclusion by *X*-ray analysis is reported in the following paper.

Table 2. *Diethyl Succinylsuccinate: Distances and angles between neighbouring molecules*

Distance[a]	Observed	Required in dimer[b]
C(1) . . . C(2′^{b})	3.58 Å	1.6 Å
C(3) . . . O(1^{b})	3.54 Å	2.8 Å
C(3) . . . C(4′^{b})	3.60 Å	3.0 Å
C(3) . . . C(3^{b})	4.25 Å	3.8 Å
Angle	**Observed**	**Required in dimer[b]**
C(1) – C(2) . . . C(1′^{b})	103.4°	90°
C(2) – C(1) . . . C(2′^{b})	76.6°	90°
C(3) . . . C(3^{b}) . . . C(3′^{b})	79.9°	90°

[a] C(3^{b}) is related to C(3) by the $+b$ translation.
C(3′^{b}) is related to C(3) through the inversion center at (0, $^1/_2$, 0).

[b] Values taken from a crude model built with 'Framework Molecular Models'.

Experimental Part. – *Data collection.* Colourless crystals of DESS were obtained by recrystallization from ethanol[5]. A suitable crystal of dimensions 0.36 × 0.32 × 0.05 mm^3 was glued to the tip of a *Lindemann* glass capillary tube. After preliminary rotation, *Weissenberg* and precession photographs it was mounted on a *Picker*-FACS-I automatic diffractometer. Cell dimensions were obtained from a least-squares fit to 2 Θ values for 12 reflections with 2 $\Theta > 32°$; they are given in Table 3. The crystal density was measured by flotation. Intensities were measured using Mo$K\alpha$ radiation with a graphite monochromator and continous Θ-2Θ scans of 1° (2Θ) per min; backgrounds were counted for 20 s at the extrema. Three reference reflections (005, 402, 020) were monitored every 28 reflections; their intensities decreased by about 7.7% during the data-collection run. All reflections in one half of reciprocal space ($l \geq 0$) out to $2\Theta = 65°$ were surveyed; they numbered 2194, of which 1754 with $I \geq 2\sigma$ (I) were accepted as observed. Observational variances σ^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 crystal decay as indicated by the reference reflections and for Lorentz and polarization effects, and reduced to structure amplitudes, F_{obs} · No absorption correction was applied (μr_{max} 0.06).

Table 3. *Crystal Data*[a]

Diethyl succinylsuccinate
(1,4-diethoxycarbonyl-2,5-dihydroxycyclohexa-1,4-diene) $C_{12}H_{16}O_6$
Triclinic, F.W. = 256.26

Space group $P_{\bar{1}}$ (from E value statistics)
a = 7.339 (4), b = 4.249 (4), c = 10.071 (5) Å
α = 95.14 (10)°, β = 103.28 (10)°, γ = 97.17 (10)°
V = 301.0 (6) Å^3, Z = 1, D_x = 1.41 g · cm^{-3}, D_m = 1.37 g · cm^{-3}
μ = 1.35 cm^{-1}, λ(Mo$K\alpha_1$) = 0.70926 Å
Molecular symmetry C_i

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

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[5] Powder diffraction confirmed that crystals grown from toluene or ethylacetate are identical to the specimen used in the present investigation.

Structure determination and refinement. E-value statistics [9] confirmed the presence of a center of symmetry. Positions of the seven atoms C(1–4) and O(1–3) were derived from a sharpened (E^2) *Patterson* map, and the two remaining carbon atoms were found from an electron density map. Block diagonal least-squares refinement of the coordinates and anisotropic temperature parameters of the nine heavy atoms led to an R ($= \Sigma |F_{obs}| - |F_{cal}|| / \Sigma |F_{obs}|$) index of 0.089 for the 1754 observed reflections. Positions of the eight hydrogen atoms were taken from a three-dimensional

Table 4a. *Diethyl Succinylsuccinate: Fractional coordinates and their estimated standard deviations*[a])

Atom	x/a	y/b	z/c
O(1)	−0.30093 (9)	0.27311 (18)	−0.13237 (6)
O(2)	−0.38984 (11)	0.36175 (22)	0.10378 (7)
O(3)	−0.20781 (9)	0.19434 (16)	0.28595 (6)
C(1)	−0.12543 (12)	0.11861 (21)	0.07568 (7)
C(2)	−0.15881 (11)	0.14231 (20)	−0.06053 (7)
C(3)	−0.04053 (11)	0.02062 (20)	−0.15035 (7)
C(4)	−0.25398 (12)	0.23541 (21)	0.15247 (8)
C(5)	−0.33383 (15)	0.30432 (28)	0.36600 (10)
C(6)	−0.25301 (18)	0.26069 (32)	0.51228 (10)
H(3A)	−0.1270 (16)	−0.1446 (28)	−0.2193 (12)
H(3B)	−0.0010 (17)	0.2013 (28)	−0.2004 (12)
H(O)	−0.3632 (24)	0.3413 (42)	−0.0673 (19)
H(5A)	−0.4611 (20)	0.1667 (33)	0.3305 (15)
H(5B)	−0.3378 (20)	0.5300 (35)	0.3562 (16)
H(6A)	−0.1226 (24)	0.3986 (40)	0.5515 (17)
H(6B)	−0.2341 (24)	0.0371 (40)	0.5227 (18)
H(6C)	−0.3370 (22)	0.3288 (37)	0.5673 (17)

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

Table 4b. *Diethyl Succinylsuccinate: Thermal Parameters*

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{31}
O(1)	0.01611	0.06900	0.00610	0.03713	0.01190	0.00548
O(2)	0.02023	0.09171	0.00832	0.05514	0.01872	0.01082
O(3)	0.01663	0.06067	0.00539	0.02649	0.00554	0.00789
C(3)	0.01272	0.04239	0.00505	0.01711	0.00441	0.00523
C(2)	0.01237	0.04164	0.00526	0.01670	0.00562	0.00426
C(1)	0.01426	0.04942	0.00456	0.02299	0.00540	0.00446
C(4)	0.01408	0.04748	0.00564	0.01905	0.00569	0.00630
C(5)	0.01987	0.07591	0.00727	0.03099	0.00431	0.01239
C(6)	0.02606	0.08720	0.00643	0.01749	0.00280	0.01219

Atom	B
H(3A)	1.42
H(3B)	1.63
H(0)	4.69
H(5A)	3.27
H(5B)	3.13
H(6A)	4.38
H(6B)	4.82
H(6C)	3.26

The anisotropic temperature factor is defined by

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

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.

We thank Prof *H. Batzer* and Dr *J. Sinnreich* for suggesting the problem and supplying the crystals, and *W. Thäsler* and *H. R. Walter* for technical assistance.

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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, $C_{24}H_{32}O_{12}$, 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].