Tetrahedron Vol. 36, pp. 3421 to 3425
Pergamon Press Ltd., 1980. Printed in Great Britain

PHOTOCHEMICAL REACTIONS—XXXV[1]

TOPOCHEMICAL AND NONTOPOCHEMICAL CONTROL IN THE CRYSTALLINE STATE PHOTODIMERIZATION OF A GIBBERELLIN ENONE. CRYSTAL AND MOLECULAR STRUCTURE OF 3-DEHYDRO GIBBERELLIN A$_3$ METHYL ESTER

L. KUTSCHABSKY, G. RECK and E. HÖHNE
Central Institute for Molecularbiology of the Academy of Sciences of the GDR, Berlin-Buch, GDR

and

B. VOIGT and G. ADAM*
Institute for Plant Biochemistry of the Academy of Sciences of the GDR, Halle (Saale), GDR

(*Received in Germany* 28 *April* 1980)

Abstract—In connection with studies concerning the solid state photochemistry of the 3-dehydro gibberellin A$_3$ system **1**, the crystal and molecular structure of the methylester **1b** has been determined by X-ray analysis. The lattice parameters are $a = b = 9.848$ Å and $c = 35.955$ Å; the space group is $P4_12_12$. The final discrepancy factor R is 0.081. The photoreactivity of **1b** has been correlated with the molecular packing arrangement allowing to predict the constitution and stereochemistry of the formed main topodimer as **4**. A mechanism for the simultaneous formation of the nontopochemical minor dimer as **3** is proposed.

In earlier investigations[2] we showed the high photoreactivity of the 3-dehydro gibberellin A$_3$ type **1** in the crystalline state[3] and the striking dependence of the photochemical reaction pathway on the kind of the substituent *R*. Whereas the free enone acid **1a** upon $n \rightarrow \pi^*$ excitation of the enone chromophor undergoes intramolecular decarboxylation to the phenolic acid **2**[4] in high yield, the corresponding methylester **1b** gives two primary dimers both arising from an intermolecular $[2+2]$ photocycloaddition of the excited Δ^1 enone double bond to the terminal olefine function of an adjacent second molecule. From a multitude of regio- and stereoisomers the structures **3** and **4** have been proposed for the two dimers on the basis of physical data and stereochemical considerations.[2]

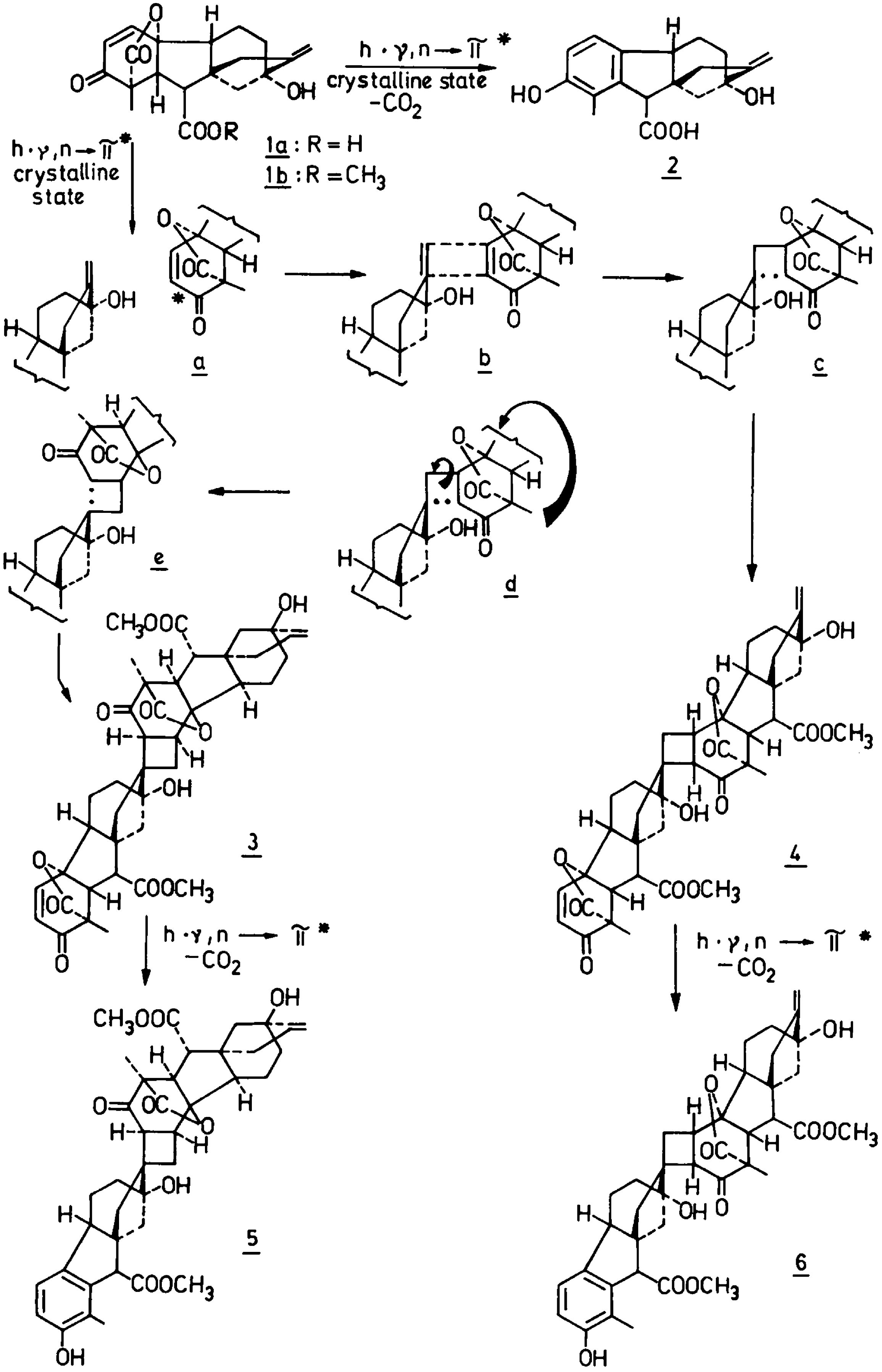
For a correlation between structure and photoreactivity, an X-ray analysis of the starting 3-dehydro gibberellin A$_3$ methylester (**1b**) has been performed and the molecular contact geometry of the monomer in its crystalline phase has been studied

For data collection a nearly rectangular parallelepipeded single crystal of compound **1b** ($C_{20}H_{22}O_6$) crystallized from aceton/hexan has been used. Crystal data: tetragonal, $a = b = 9.848(4)$, $c = 35.955(7)$ Å, $Z = 8$, $D_x = 1.363$ g cm^{-3}, space group $P4_12_12$, m.p. 189–192°C, $[\alpha]_D^{26}$ + 67.2° (ethanol). The intensities of 1279 independent reflections were measured on a Hilger-Watts four-circle diffractometer within a 2Θ sphere of 43°, using graphite-monochromated MoK$_\alpha$ radiation and a Ω/2Θ scan mode. Corrections for Lorentz and polarization effects were carried out in the usual way. No absorption and extinction corrections were applied.

The structure has been solved by direct methods using 297 normalized structure factors (*E*-values with $|E| > 1.2$) with the help of the CORDAL-method[5] and subsequently the program MULTAN 74[6]. The *E*-map computed from the set with the best consistency produced the model of the molecule, which fitted the geometry of the title compound **1b** and revealed the positions of all non-hydrogen atoms. Full-matrix least-squares refinement with the program SHELX 76[7] with individual isotropic temperature factors reduced the discrepancy factor *R* to 0.11. A difference Fourier map gave the positions of the hydrogen atoms. The subsequent anisotropic refinement of the non-H atoms,

Table 1. Positional parameters (ESD in parentheses)

Atom	x/a	y/b	z/c
C(1)	1.0589 (8)	0.5307 (9)	0.2656 (2)
C(2)	1.0678 (9)	0.6381 (9)	0.2431 (2)
C(3)	0.9798 (9)	0.7577 (9)	0.2479 (2)
C(4)	0.8944 (8)	0.7617 (8)	0.2841 (2)
C(5)	0.9707 (8)	0.6844 (8)	0.3149 (2)
C(6)	0.9009 (7)	0.6729 (8)	0.3526 (2)
C(7)	0.9465 (8)	0.7793 (8)	0.3795 (2)
C(8)	0.9278 (7)	0.5239 (8)	0.3660 (2)
C(9)	0.9858 (8)	0.4489 (7)	0.3303 (2)
C(10)	0.9660 (7)	0.5428 (7)	0.2987 (2)
C(11)	0.9198 (9)	0.3049 (8)	0.3241 (2)
C(12)	0.9053 (9)	0.2248 (9)	0.3609 (2)
C(13)	0.8634 (8)	0.3184 (8)	0.3945 (2)
C(14)	0.8004 (7)	0.4485 (7)	0.3800 (2)
C(15)	1.0254 (7)	0.5061 (8)	0.3983 (2)
C(16)	0.9922 (8)	0.3670 (8)	0.4143 (2)
C(17)	1.0548 (9)	0.3056 (8)	0.4420 (2)
C(18)	0.8410 (8)	0.9036 (8)	0.2920 (2)
C(19)	0.7811 (9)	0.6598 (9)	0.2760 (2)
C(20)	0.8905 (8)	0.9015 (8)	0.4342 (2)
0(3)	0.9727 (8)	0.8459 (7)	0.2246 (2)
0(7)	1.0554 (6)	0.8321 (6)	0.3790 (1)
0(71)	0.8541 (5)	0.8039 (5)	0.4059 (1)
0(10)	0.8232 (5)	0.5342 (5)	0.2851 (1)
0(13)	0.7772 (6)	0.2388 (5)	0.4182 (2)
0(19)	0.6717 (6)	0.6833 (6)	0.2631 (2)


h · γ, n → π*
crystalline state
−CO2
1a : R = H
1b : R = CH3
2
h · γ, n → π*
crystalline state
a
b
c
d
e
3
4
h · γ, n → π*
−CO2
5
h · γ, n → π*
−CO2
6

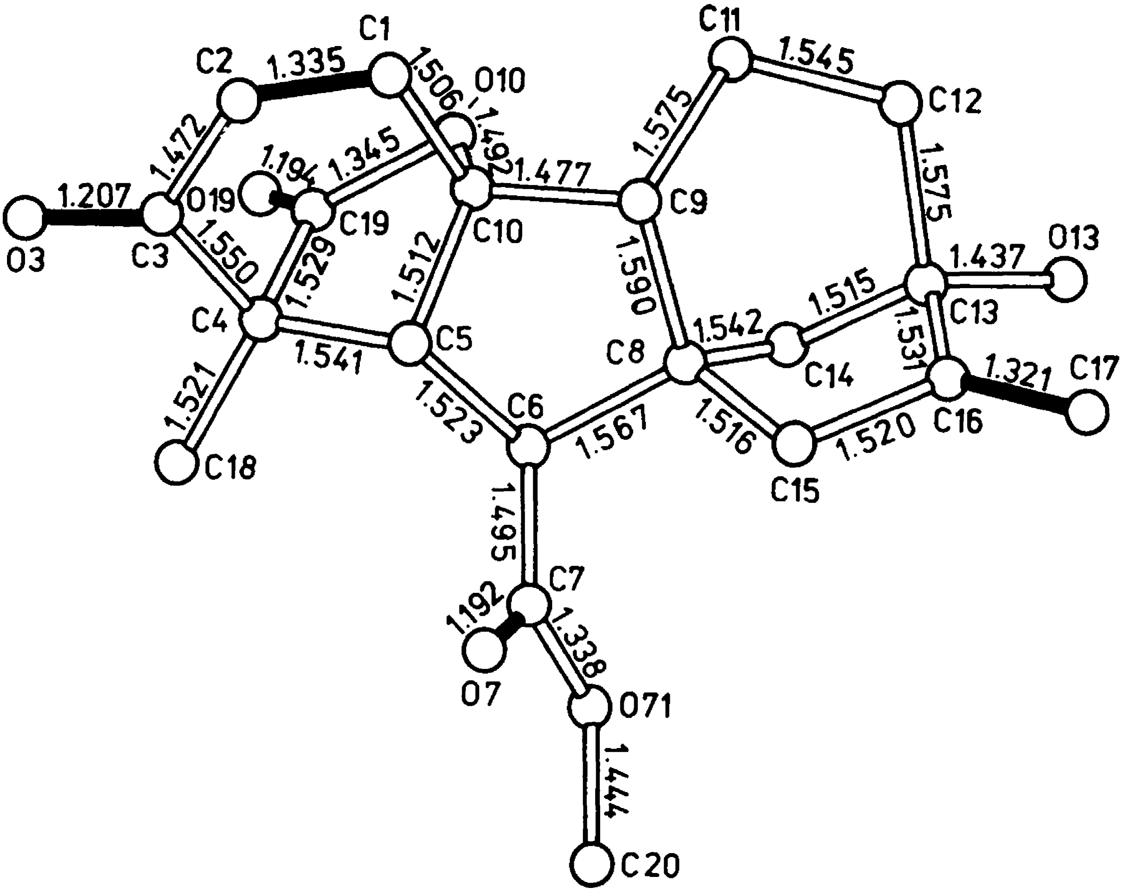


Fig. 1. Bond lengths in the structure of 3-dehydro gibberellin A_3 methylester in A. (ESD's < 0.013 Å).

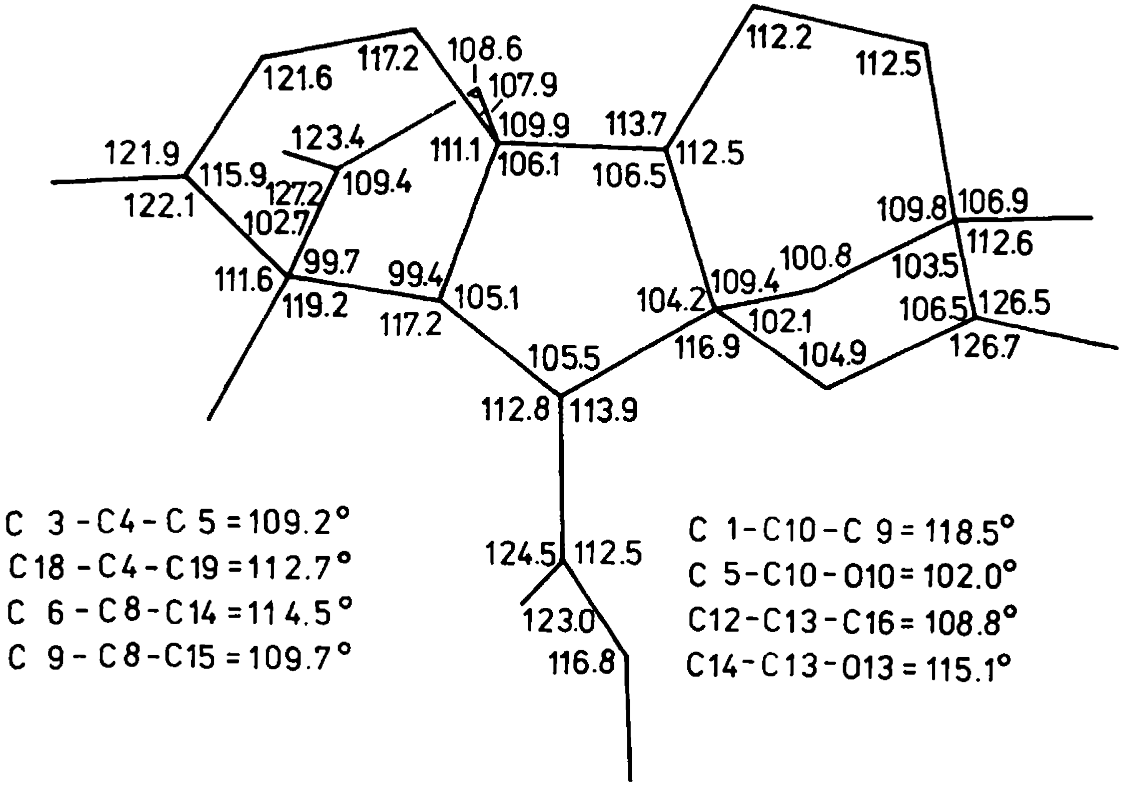


Fig. 2. Bond angles in the structure of 3-dehydro gibberellin A_3 methylester (ESD's < 0.8°).

in which unit weights were used and the parameters of the hydrogen atoms were kept fixed, led to the final value of $R = 0.081$. The final atomic positional parameters are listed in Table 1. The molecular structure including bond lengths and angles is shown in Figs 1 and 2. The estimated standard deviations for the bond distances lie between 0.009 and 0.013 Å, for the bond angles between 0.6 and 0.8°.

The intramolecular geometry of **1b** corresponds nearly to that of the free enon acid **1a.**[8] In the two structures bond lengths and angles deviate from normal values at corresponding positions with the exception of the bond C(12)-C(13). The bond length C(9)-C(10) of 1.477 Å is shortened significantly whereas the bond distances C(9)-C(11) of 1.575 Å and C(8)-C(9) of 1.590 Å are lengthened. The shortening of the C(2)-C(3) bond is due to the enone conjugation effect. The bond length C(19)-O(10) of 1.345 Å agrees well with the corresponding value of 1.34 Å observed in the structure of 3-dehydro gibberellin A_3,[8] indicating a small contribution of the resonance form $R-\underset{O^-}{\underset{|}{C}}=O^+-R$.

The conformation of the 6β-methyoxycarbonyl function is defined by the torsion angle C(5)-C(6)-C(7)-O(7) of −27.9°. The five-membered ring B exhibits a half-chair conformation in which the atoms C(5) and C(10) are displaced by 0.308 Å and −0.246 Å, respectively, to opposite sides from the plane defined by C(6), C(8) and C(9). The lactone ring has an envelope conformation.

The relative position of two molecules involved in the solid state photodimerization of **1b** is shown in Fig. 3 and characterized by a chain-like head to tail arrangement of the molecules around a fourfold screw axis. The large distances O(13)-O(19') of 3.49 and O(13)-O(3') of 3.30 Å exclude the formation of intermolecular H- bonds between these atoms so that the molecules are held together only by van der Waals interactions. The intermolecular distance between the adjacent double bonds C(16)-C(17) and C(1')-C(2') (resulting from C(1), C(2) by the symmetry operation of a four fold screw axis $0.5 - y$, $0.5 + x$, $0.25 + z$) which undergo photocycloaddition is 3.71 Å well within the range 3.5 – 4.2 Å previously observed[9,10] for such topochemical reactions. The individual values for the C(16)-C(2') and C(17)-C(1') distances are 3.69 and 3.73 Å, respectively. The π-orbitals of C(16)-C(17) and C(1')-C(2') lie nearly in a common plane and are directed towards one another. The dihedral angle between the least squares planes defined by the atom C(13), C(15), C(16), C(17) and C(1'), C(2'), C(3'), C(10') is 19.7°. The torsion angle C(17), C(1617), C(01'02'), C(1') shows a value of 31.2° (C(1617) is the midpoint between C(16) and C(17) and C(01'02') is the midpoint between C(1') and C(2'), respectively). Thus, all geometrical requirements[11] for a topochemical [2 + 2] cycloaddition in **1b** are fulfilled allowing to predict the constitution and stereochemistry of the formed main photodimer, isolated in up to 40 % yield as **4**.

In contrast to the lattice controlled formation of **4** the origin of the observed[2] minor photodimer can not be explained on the basis of the found (ideal) molecular packing of the starting enone **1b**. Therefore, this second cycloadduct must formed be due to a non-topochemical[12] photodimerization. In earlier studies it had been shown that only the structures **3** and **4** are in keeping with physical properties, whereas all others may be excluded by physical measurements and stereochemical considerations.[2] In particular a structure differing from dimer **3** by a β-arrangement of the hydrogens at C(1') and C(2') of the cyclobutane ring, which may be formed by a reaction between two different chains of molecules in the region of crystalline imperfections, can be excluded on the basis of the found[2] negative carbonyl Cotton effect. In view of these results we may conclude that **3** is the structure of the minor photodimer, given reversed as **4** in our first proposal basing on an ORD discussion.[2] Crystalline imperfections have been shown to be of importance for the explanation of such nontopochemical photodimerizations by various authors.[11–14] In some cases a rotation of monomeric molecules of an intermediate excimer in the environment of imperfections was postulated.[15,16]

From a mechanistical point of view the simultaneous formation of **3** and **4** from crystalline **1b** may be understand as a two step mechanism of the cyclobutane ring closure involving the 1.4 diradical **c** produced via an eximer **b**, as follows: Whereas direct recombination

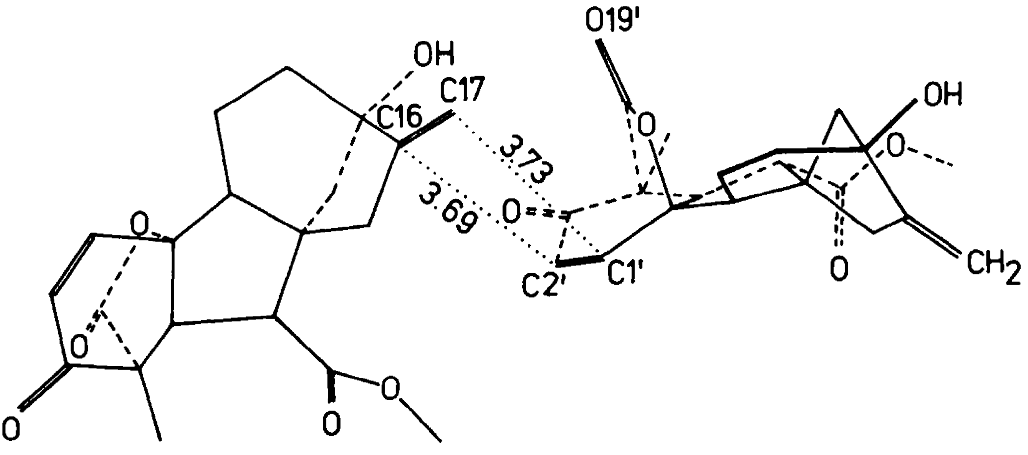


Fig. 3. Arrangement of molecules around the fourfold screw axis.

of **c** leads to the main topodimer **4**, an internal rotation of one molecular half as shown in **d** would give the rotameric 1.4 diradical **e**. Such a molecular rotation may be facilitated by the absence of any hydrogen bonds in the crystal structure of **1b**. A further photochemical reaction of the two primarily formed dimers **3** and **4** via excitation of the remaining enone chromophor leads under intramolecular decarboxylation to the ring A phenolic dimers **5** and **6**, respectively.[2,17]

The dimerization of **1b** in the crystalline state is in remarkable contrast to the photochemical behaviour of the free enone acid **1a** which leads upon irradiation in the crystalline state to the phenolic acid **2**.[4] As shown by an earlier X-ray study of **1a**[8] such a striking different photochemical behaviour results from the different molecular packing arrangement of the free acid **1a** in the crystalline state. In contrast to **1b** the molecules of **1a** form sheets connected by hydrogen bonds. In the monoclinic crystal structure of **1a** the distance between the terminal C(16)–C(16) olefinic group of one molecule and the adjacent C(1′) C(2′) bond of another molecule is 4.5 Å and the corresponding π-orbitals are arranged nearly orthogonal, so that only intramolecular photochemical reactions can take place.

Acknowledgements The authors thank Prof. Dr. habil. K. Boll-Dornberger for stimulating discussions and Dr. R.-G. Kretschmer for provision and adaption of computer programs.

REFERENCES

[1] Part XXXIV: M. Lischewski, G. Adam and E. P. Serebryakov, *Tetrahedron Letters* 45 (1380); *Gibberellins*—LXXIV, Part LXXIII, see before.

[2] G. Adam, *Tetrahedron* **29**, 3177 (1973).

[3] For the various photochemical reaction pathways of type **1** in solution see B. Voigt and G. Adam, *Ibid.* **32**, 1581 (1976); and refs. cited.

[4] G. Adam and B. Voigt, *Tetrahedron Letters* 4601 (1971).

[5] L. Kutschabsky, G. Reck, S. Kulpe and E. Höhne, *Kristall und Technik* **10**, 731 (1975).

[6] P. Main, M. M. Woolfson, L. Lessinger, G. Germain and I. P. Declercq: *Multan* 74. A *System of Computer Programs for the Automatic Solution of Crystal Structures*, Univ. of York, England and Louvain, Belgium (1974).

[7] G. M. Sheldrick, *SHELX* 76 *Program for Crystal Structure Determination*, Univ. York, England (1976).

[8] L. Kutschabsky, G. Reck and G. Adam, *Tetrahedron* **31**, 3065 (1975).

[9] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.* 1996 (1964).

[10] G. M. J. Schmidt, *Pure Appl. Chem.* **27**, 647 (1971).

[11] M. D. Cohen, *Angew. Chem.* Internat. Edit. **14**, 386 (1975).

[12] E. Heller and G. M. J. Schmidt, *Israel J. Chem.* **9**, 449 (1971).

[13] M. D. Cohen and B. S. Green, *Chem. Brit.* **9**, 490 (1973).

[14] J.-P. Desvergne, F. Chekpo and H. Bouas-Laurent, *J. Chem. Soc.* Perkin II 84 (1978) and refs cited.

[15] A. Kawada and M. M. Labes, *Mol. Cryst. Liq. Cryst.* **12**, 133 (1970).

[16] E. J. Baum in J. N. Pitts, Jr., *Excited State Chemistry*, p. 121. Gordon & Breach, New York (1970).

[17] G. Adam, L. Kutschabsky and G. Reck, *Proc.* VII. *IUPAC Symp. on Photochemistry*, 24. 28. 7. 78 at Leuven, p. 9.