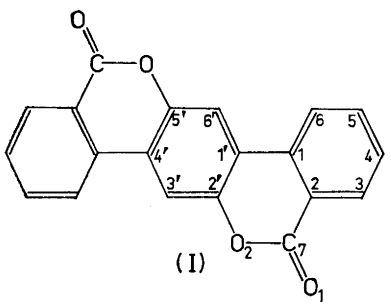
The Crystal and Molecular Structure of 2′,5′-Dihydroxyterphenyl-2,2″-dicarboxylic Acid Dilactone

BJÖRN PEDERSEN

Kjemisk institutt, Universitetet i Oslo, Blindern, Norway

As shown by Bernatek [1] the compound, $C_{18}H_{10}O_4$, formed by briefly heating an alkaline solution of methylphenylglyoxal-*o*-carboxylic acid probably is 2′,5′-dihydroxyterphenyl-2,2″-dicarboxylic acid dilactone (I).



(I)

To get further support for the assumed formula an X-ray crystallographic study of the compound was undertaken. The crystals, recrystallised from nitrobenzene, were long, very thin needles. Oscillation and Weissenberg photographs taken with Cu*K*-radiation (λ = 1.540 Å) showed the crystals to be monoclinic with

$$a = 3.82 \text{ Å} \quad b = 14.11 \text{ Å} \quad c = 12.54 \text{ Å}$$
$$\beta = 94.0°$$

The needle axis of the crystals is parallel to the *a*-axis. Systematic absences. *h0l* when *l* is odd, *0k0* when *k* is odd. This unambiguously determines the space group as No. 14, $P2_1/c$. The observed density [1], 1.53 g/cm³, indicates the presence of two formula units in the unit cell (d_{calc} = 1.55 g/cm³). The space group symmetry requires that the molecule possesses a centre of symmetry. Furthermore the short *a*-axis shows that the molecule is nearly planar (van der Waals thickness of an aromatic nucleus is 3.70 Å [2]). All this fully supports the formula (I).

The molecule must consequently lie in the unit cell nearly parallel to the *a* plane with its centre of symmetry in the origin. The only parameter left to determine before the molecule is located completely in the unit cell is therefore the angle the molecule is turned out from the *b* or *c*-axis. Due to these simplifying features of the crystal structure a quantitative investigation of the [100]-projection could be carried out. The intensities of the *0kl*-reflexions (109 out of 258 theoretically accessible) were measured with a photometer from integrated Weissenberg photographs taken with Cu*K*-radiation. The intensities were corrected for Lorentz and polarisation effects but not for absorption and extinction. On the basis of the corrected $F(0kl)$ [2]-values a Patterson map was worked out. The map showed a marked peak near the origin, at $v = 0.131$, $w = 0.123$, which probably is due to the intramolecular vector between O_1 and O_2 and coinciding O—C and C—C vectors. This reduces the possible ways of placing the molecule in the projection to two: the benzene ring 1—6 may either be placed near the *b*- or the *c*′-axis. But as $|F(021)|$ is very large and almost twice $|F(012)|$ the benzene ring must be placed near the *c*′-axis. A set of signs were calculated on the basis of a planar molecule analogous to (I) with all atoms equal and all nearest neighbour distances

Table 1. Atomic coordinates as fractions of the corresponding cell edge and the temperature factor *B* (in $\exp(-B\sin^2\Theta/\lambda^2)$).

Atom	*y*	*z*	*B*
C_1	0.060	0.205	3.2
C_2	0.155	0.234	3.1
C_3	0.190	0.334	4.7
C_4	0.129	0.405	4.3
C_5	0.032	0.377	4.7
C_6	−0.004	0.278	3.7
C_7	0.223	0.157	3.9
C_1'	0.026	0.103	2.4
C_6'	−0.070	0.070	3.3
C_2'	0.092	0.033	3.5
O_1	0.305	0.174	3.3
O_2	0.186	0.062	2.8

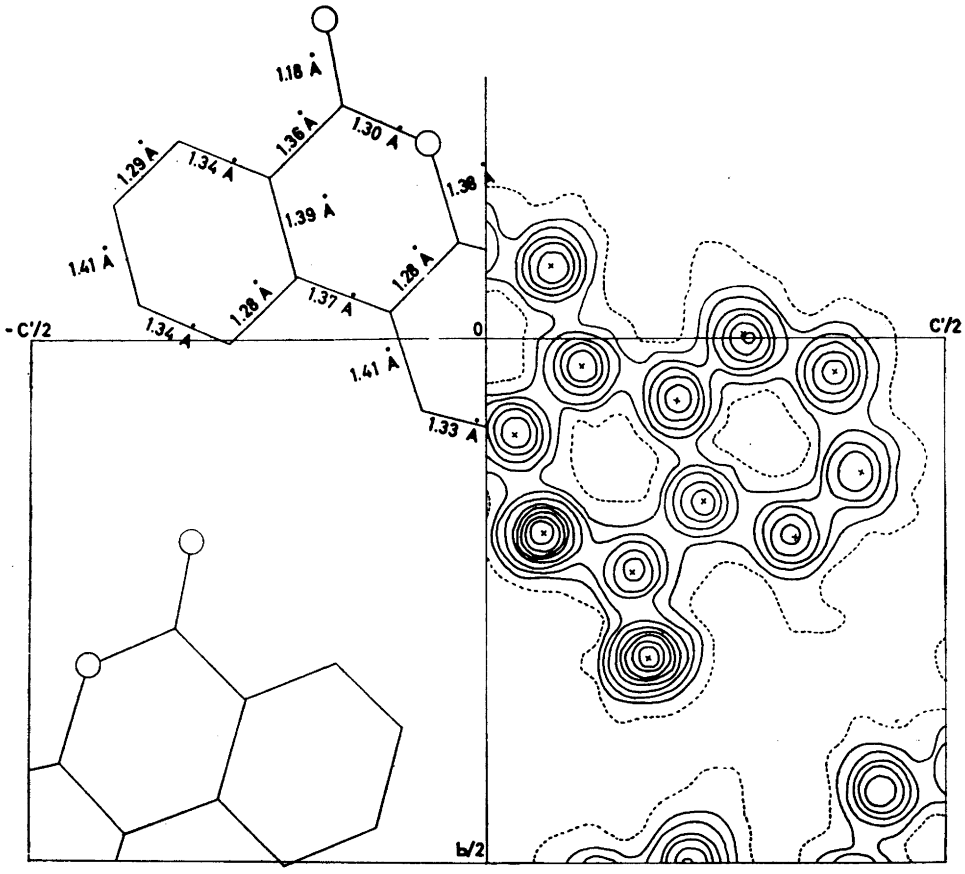


Fig. 1. *a*-Axis Fourier projection of $C_{20}H_{10}O_4$ with the found interatomic distances in the projection. Contours at intervals of 1 eÅ^{-2} with the 1 eÅ^{-2}-line broken.

equal to 1.40 Å in this position. A Fourier projection was evaluated, and this clearly showed all the atoms well resolved with the electron density in the oxygen positions distinctly higher than in the rest of the atomic positions. The atomic coordinates which were derived from the Fourier projection, were refined by the method of least squares on the Ferranti Mercury computer "Fredric" at the Norwegian Defence Research Establishment. The refinement was terminated after five cycles. The final coordinates and individual temperature factors, B, are given in Table 1. The reliability index, R, is 0.092 (unobserved reflexions not included).

The found interatomic distances in the projection are given in Fig. 1 together with the final Fourier map. The figure shows that the molecule is tilted somewhat out of the [100]-projection plane. The found projected bond distances indicate that the terphenyl part of the molecule is planar or nearly so with the carbonyl oxygen and lactone oxygen a little twisted out on each side of this plane. From such a model of the molecule and an assumed C—C distance in the terphenyl part of 1.40 Å the true C_2-C_7 and $C_1-C_{1'}$ distance are calculated as 1.48 Å and 1.43 Å, respectively. The former of these is in good agreement with what is found [3] for the corre-

sponding distance in benzoic acid, 1.48 Å. The Fourier map in Fig. 1 shows that the electron density in the carbon positions decreases with the distance from the origin, *i. e.* the centre of symmetry of the molecule. The temperature factors, B, increase in the same order. This is in accordance with what is found in other planar centrosymmetric molecules as naphthalene [4] and anthracene [5] and is due to the rigid-body vibrations of the molecules [6]. — The molecular packing is similar to the arrangement found in 1,2,5,6-dibenzanthracene [7].

1. Bernatek, E. *Acta Chem. Scand.* **13** (1959) 1719.
2. Ketelaar, J. A. A. *Chemical Constitution*, 2. Ed. Elsevier, Amsterdam 1958.
3. Sim, G. A., Robertson, J. M. and Goodwin, T. H. *Acta Cryst.* **8** (1955) 157.
4. Abrahams, S. C., Robertson, J. M. and White, J. G. *Acta Cryst.* **2** (1949) 238.
5. Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 915.
6. Cruickshank, D. W. J. *Revs. Modern Phys.* **30** (1958) 163.
7. Robertson, J. W. and White, J. G. *J. Chem. Soc.* **1947** 1001.

Received September 18, 1959.

The Fatty Acid Composition of Shea Butter and Olive Kernel Oil

AAGE JART

Danish Fat Research Institute, Copenhagen, Denmark

Shea butter. Shea butter (or karite butter) comes from the seeds of *Butyrospermum Parkii* of the family *Sapotaceae*. After the second world war shea nuts have been imported into Europe on a relatively small scale, but in Denmark the oil is used in appreciable quantities for certain types of margarines. It would therefore be of interest to know the composition of the fatty acids of this oil and especially the content of essential fatty acids.

For the present investigation shea nuts from West Africa were used. The fat in the nuts was isolated and analyzed, *i. a.* by alkali isomerization [1] and — in the form of methyl esters — by quantitative gas-liquid chromatography [2]. The chromatograph used was supplied by Griffin & George and had a 0.9 m column (25 % silicone grease on 40—60 mesh Firebrick). The temperature of the column was 215°C, the outlet pressure 1 atm, the katharometer current 100 mA, and the carrier gas used was helium (1.0 l/h). Using a speed of the recorder paper of 6 inches/h, the quantity M (in μl) of the individual components of the methyl ester mixture could be determined from the area A (in cm²) lying under the corresponding peaks in the chromatogram by applying the following formula (which has been derived by calibrating the apparatus by means of pure fatty acid methyl esters):

$$M_i = \log_{10}^{-1} (0.889 \times \log_{10} (A_i) - 0.058)$$

The calculated fatty acid composition (in weight per cent of the fatty acid mixture) and other results obtained from the analyses of the shea butter appear from Table 1; the content of oleic acid is found by determining the iodine value, while the stearic acid percentage is obtained as a difference. The results are in good agreement with those published in earlier works [3,4].

Olive kernel oil. Olive oil is obtained from the fruits of *Olea europea* which belongs to the family *Oleaceae*. The olive kernel contains about 1 % of the total amount of oil in the olive. Olive oil usually contains the kernel oil, as the olive stones are generally crushed during the milling procedure to which the olives are subjected in the factories. As adequate information concerning the linoleic acid content of olive kernel oil was not available from the literature, an investigation of this oil has been carried out.

The fatty acid composition *etc.* was determined in oil isolated from the kernels of olives obtained from Morocco. The investigation was made in the same manner as in the case of shea butter, and the results are summarized in the last column of Table 1. The oil examined showed a higher degree of unsaturation than a Portuguese olive kernel oil examined previously [5]. The composition ascertained is in fairly good agreement with that given for an olive kernel oil from the U.S.A. [6]