Tetrahedron Letters No.21, pp. 2527-2529, 1968. Pergamon Press. Printed in Great Britain.

THE GEOMETRY OF THE BENZENE RING IN 1,2,4,5-TETRA-TERTIARYBUTYLBENZENE

A.van Bruijnsvoort, L.Eilermann, H.van der Meer
and C.H.Stam

Laboratory for Crystallography, Nieuwe Prinsengracht 126
Amsterdam, The Netherlands

(Received in UK 16 February 1968; accepted for publication 26 February 1968)

It has been a point of discussion for some time in how far t-butyl groups in ortho position cause distortion of a benzene ring, See, for instance, Hoogzand and Hübel (1), Dale (2). In order to obtain direct information on this point a crystal structure determination of 1,2,4,5-tetra-t-butylbenzene was undertaken.

1,2,4,5-tetra-t-butylbenzene crystallizes in an orthorhombic and a monoclinic modification. The monoclinic crystals were used in our investigation. They have the following cell constants :

$a = 10.910$
$b = 9.988$ all ± 0.001 Å $\beta = 112.3 \pm 0.1^\circ$
$c = 10.051$

The space group is $P2_1/n$ and there are two molecules in the unit cell; the molecules, therefore, have a centre of symmetry.

The main features of the structure were derived from a threedimensional Patterson synthesis, except for the positions of the methyl groups, which were found from subsequent electron density calculations. The structure has been refined by least squares methods to a discrepancy factor $R = 9.4\%$ for 1026 observed reflexions.

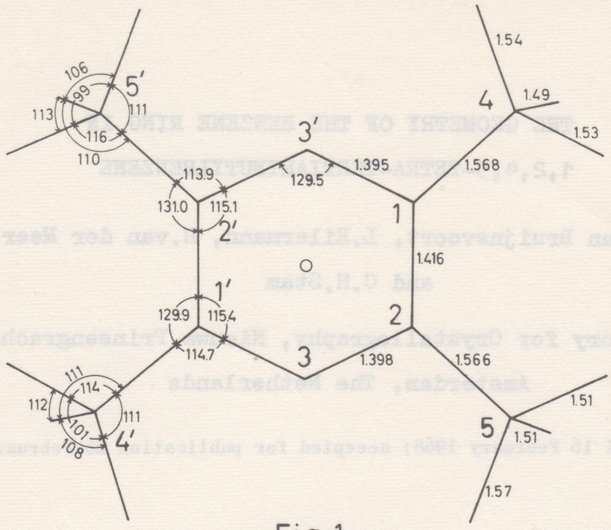

Fig.1

We only want to report the results pertinent to the geometry of the benzene ring. In Fig.1 the bond distances and interbond angles of the carbon skeleton are indicated. From the bond angles around the ring atoms it is quite clear that considerable strain must exist in the molecule. The planarity, however, has not been affected, as can be seen from Table 1. As the calculated positional standard deviations for the ring atoms and the adjacent atoms are 0.005 and 0.006 Å respectively, the deviations from the best planes are not significant. Apparently, the intramolecular strain is relieved by angle deformation rather than by out of plane distortion of the ring. The mutual repulsion of the t-butyl groups in ortho position causes an increase in the angles C(2)C(1)C(4) and C(1)C(2)C(5) from the unstrained value of 120° to about 130°. As a result the remaining angles around C(1) and C(2) are decreased by about 5°, and, since the ring stays planar, the angle C(2)C(3)C(1') has to increase to about 130°.

Similar results as to the effect of steric interaction on conjugated systems have been found with Vitamin-A-acid (3), 15,15'-dehydro-β-carotene (4), 7,7'-dihydro-β-carotene (5) and other carotenoid compounds (6), where the steric interaction of the methyl groups in the conjugated chain with this chain causes it to be bent in its own plane without much out of plane distortion.

The bonds connecting the t-butyl groups with the ring are long compared with similar bonds in other compounds. For toluene, for instance, a value of 1.51 ± 0.02 Å for the $C-CH_3$ bond has been reported (7).

The interbond angles within the two independent t-butyl groups show a consistent pattern which may be understood in terms of the steric interaction of the t-butyl groups.

Full details of the crystal structure will be given elsewhere.

Table 1

Distances in Å of

1. Ring atoms from the best plane through the benzene ring (column 2)
2. Ring and adjacent atoms from their best plane (column 3)

C(1)	-0.005	-0.005
C(2)	+0.005	+0.011
C(3)	-0.005	+0.001
C(4)	-	+0.002
C(5)	-	-0.005
C(1')	+0.005	+0.005
C(2')	-0.005	-0.011
C(3')	+0.005	-0.001
C(4')	-	-0.002
C(5')	-	+0.005

Our thanks are due to Dr.C.Hoogzand for suggesting the investigation and providing the crystals.

References

1. C.Hoogzand and W.Hübel, Tetrahedron Letters, 18, 637 (1961)
2. J.Dale, Chem. Ber., 94, 282 (1961)
3. C.H.Stam and C.H.MacGillavry, Acta Cryst., 16, 62 (1963)
4. W.Sly, Acta Cryst., 17, 511 (1964)
5. C.Sterling, Acta Cryst., 17, 500 (1964)
6. J.C.J.Bart and C.H.MacGillavry, Acta Cryst., 21, A103 (1966)
7. F.A.Keidel and S.H.Bauer, J.Chem.Phys., 25, 1218 (1956)