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CRYSTAL AND MOLECULAR STRUCTURE OF 2,5-DIMETHYL-3,4-DI(2-PROPYL)-HEX-3-ENE (TETRAISOPROPYLETHYLENE) AT 170 K.

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Summary: X-ray analysis of tetraisopropylethylene has revealed that the structure is disordered since there are two molecules (population factors 0.85 and 0.15 respectively) rotated by 90° with respect to each other around the normal to the ethylenic plane through the origin, which is the midpoint of the C-C double bond The ethylenic skeleton is planar and bond angles and distances are in the normal range.

This crystal structure investigation has been undertaken as part of a study of the deformations from planarity (if any) and the variations in bond distances and angles experienced in overcrowded ethylenes.(1)

Crystal Data: $C_{14}H_{28}$, MW=196.4, triclinic, space group $P\bar{1}$, a=6.4180(7), b=7.5898(9), c=7.8480(8) Å, α=80.43(1), β=70.07(1), γ=70.56(1) °, Z=1, D_m not measured, D_c=0.964 Mgm^{-3}, μ(MoKα)=0.057 mm^{-1}, F(000)=112. Cell dimensions were obtained by a least-squares fit to $\sin^2\theta$ values of 31 hkl reflexions measured on a computer controlled four-circle diffractometer. The centric space group $P\bar{1}$ was suggested by intensity statistics and fully confirmed by the successful structure determination. Since the substance quickly sublimes at room temperature, diffraction data were collected at 170 K. A variable θ-2θ scan technique was employed in intensity measurements to a maximum 2θ value of 55° (MoKα radiation, λ=0.71069 Å, graphite monochromator). Background measurements were taken at both ends of the scan range, each for a time equal to one-half the scan time. Two standard reflexions were checked every 48 intensity measurements and did not change their intensities significantly. 1568 reflexions were measured of which 1530 having scan count greater than background were treated as observed. Each reflexion was assigned a variance $\sigma^2(I)=\sigma^2(I)_{c.s.}+(0.03S)^2$, where S is the scan count. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption ($\mu=0.057$ mm^{-1} for MoKα radiation). The structure was solved by the Patterson technique. The positions of H atoms were obtained from difference syntheses. After few cycles of full-matrix least-squares refinement, apparent convergence was reached at a R value of 0.084. A difference Fourier synthesis was then computed and on the corresponding map a residual peak as large as 1.5 e/Å^3 was noticed on the ethylenic plane, 0.7 Å away from the origin on the normal to the ethylenic bond. This finding suggested that a second molecule is present which is rotated by about 90° with respect to the first one around the normal to the ethylenic plane through the origin. The situation is schematically shown in Fig. 1, from which it is clear that C1R is the only atom of the second molecule which can be distinguished unequivocally from those of the first one, the separation between the others being too small. The positional and thermal parameters of all the atoms of the second molecule (molecule II) were then calculated by rotation of the corresponding atoms of the first molecule (molecule I) by 90° around the x axis. Structure factors calculations indicated the best population factor to be 0.85 for molecule I and 0.15 for molecule II. Final refinement was accomplished by performing three full-matrix least-squares cycles including 120 parameters in a single matrix: coordinates and anisotropic coefficients b_{ij} for C atoms, coordinates and isotropic B values for H atoms of molecule I and a scale factor. The positional and thermal parameters of molecule II, including H atoms, were used in structure factors calculation but not refined. This procedure is equivalent to a refinement with the constraint that molecules I and II are identical and perpendicularly oriented. The function minimized was $\Sigma w(|F_o|-k|F_c|)^2$ with weights $w=4F_o^2/\sigma^2(F_o^2)$. The final values of the residuals were R=0.055 for the 1530 observed reflexions (0.057 including unobserved), R_w=0.071 with a goodness-of-fit 2.8. A view of the molecule is given in Fig. 1, together with the numbering scheme;

it is evident that the molecule shows 2/m symmetry. Bond lengths and angles are reported in Table 1. There is no distortion from planarity in the ethylenic skeleton and the C1-C1', C1-C2, C1-C3 distances are in the expected range, indicating that no variation in bond lengths is caused by the isopropyl groups. A typical feature of the structure is the enlargement of the C1'-C1-C2 and C1'-C1-C3 angles and the related narrowing of the C2-C1-C3 angle. These deviations from the equilibrium value of 120° are due to the interactions C2..C3' (3.04 Å), C1..C6' (3.25 Å), C1..C7' (3.25 Å), C3..H2' (2.59 Å), H2..H6B' (2.13 Å) and H2..H7B' (2.06 Å). No packing distance is less than the sum of Van der Waals radii (r_C=1.7 and r_H=1.2 Å) for molecule I. For molecule II there are three short intermolecular contacts: C5R with H3R' in x, 1+y, z (d=2.87 Å), H3R with H5AR' in x, 1+y, z (d=2.33 Å) and H4AR with H5AR' in x, 1+y, z (d=2.17 Å). These distances can be due to the fact that, actually, molecule II is not rotated by 90° exactly or its geometry is slightly different from that of molecule I and/or could explain the different values of the population factor. The geometry obtained in the present work is in excellent agreement with the results obtained by force field calculations(2) as shown in Table 2. Coplanarity of C1',C1,C2,C3, H2,H3 atoms found by the above mentioned calculations is confirmed by our result.

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Table 1. Bond lengths and angles with their e.s.d.'s. C-C-H and H-C-H angles range from 98 to 113° with e.s.d.'s in the range 1-3°.

C1-C1'	1.347(2)	C4-H4B	0.92(3)	C1'-C1-C2	122.2(2)
C1-C2	1.526(3)	C4-H4C	0.85(4)	C1'-C1-C3	125.2(2)
C1-C3	1.531(3)	C5-H5A	1.01(3)	C2-C1-C3	112.6(1)
C2-C4	1.532(2)	C5-H5B	0.92(3)		
C2-C5	1.528(3)	C5-H5C	0.85(4)	C1-C2-C4	112.5(2)
C3-C6	1.533(3)	C6-H6A	0.95(3)	C1-C2-C5	112.2(2)
C3-C7	1.527(3)	C6-H6B	0.88(3)	C4-C2-C5	110.8(1)
		C6-H6C	0.97(3)		
C2-H2	1.00(2)	C7-H7A	0.92(3)	C1-C3-C6	114.3(1)
C3-H3	1.02(2)	C7-H7B	0.85(3)	C1-C3-C7	114.5(2)
C4-H4A	0.97(3)	C7-H7C	0.98(3)	C6-C3-C7	112.8(2)

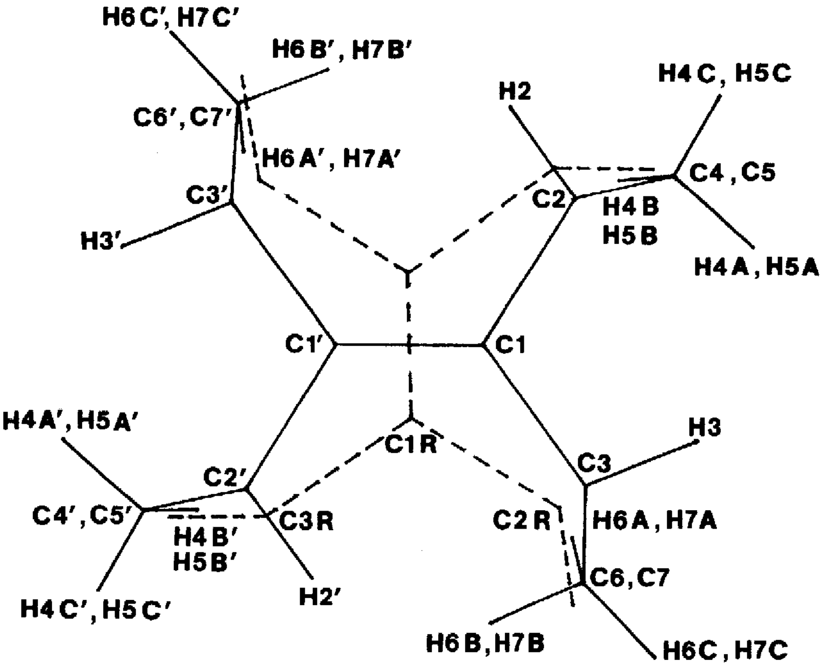

Fig. 1. View of tetraisopropylethylene molecule along a principal axis of inertia. Full line molecule I; dashed line molecule II (only C atoms).

Table 2. Comparison of calculated and experimental geometries. Bond lengths in Å, bond angles in degrees.

	ref. (2)	present work		ref. (2)	present work
C1-C1'	1.347	1.347	C1-C2-C4	112.2	112.5
C1-C2	1.527	1.526	C1-C2-C5		112.2
C1-C3	1.527	1.531	C1'-C1-C3	125.2	125.2
C1-C3-C6	113.6	114.3	C1'-C1-C2	123.2	122.2
C1-C3-C7		114.5	C1-C3-H3	107.5	105.
			C1-C2-H2	110.6	111.

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