

Short Communications

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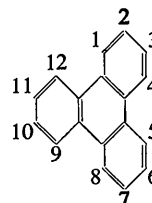
Preliminary crystallographic data for methyl-substituted triphenylenes. By J. YERKES, D. W. JONES and W. A. DENNE,* *School of Chemistry, University of Bradford, Bradford, 7, Yorkshire, England*

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Unit-cell dimensions and space groups are reported for six methyl-substituted triphenylenes: 1-methyl, 2-methyl, 1,3-dimethyl, 1,6,11-trimethyl, 1,3,6,11-tetramethyl, and 2,3,6,7,10,11-hexamethyl. The average volume per methyl group added decreases only slightly with successive substitution.

As a complement to a programme of investigation of steric effects on nuclear magnetic resonance chemical shifts of polycyclic aromatic hydrocarbons in solution (see, e.g. Bartle & Jones, 1967, 1969; Bartle, Heaney, Jones & Lees, 1966), preliminary crystallographic data have been determined for the six methyl-substituted triphenylenes shown in Table 1. For comparison, corresponding data for the parent hydrocarbon (Ahmed & Trotter, 1963) are also listed. Cell dimensions were derived from rotation photographs and zero- and first-layer line Weissenberg photo-

graphs taken with Cu $K\alpha$ radiation. In the absence of corrections for systematic film-shrinkage errors, the accuracy is limited to about 1%. Densities were measured by flotation in aqueous solutions of sodium iodide.



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Table 1. *Unit-cell data for methyl-substituted triphenylenes, together with Trotter's (1963) data for triphenylene*

Substituent (and reference to source)	System and space group	Unit-cell dimensions*	Unit-cell volume (\AA^3)	Density (g.cm^{-3})		Molecules per cell	Vol. (\AA^3) per methyl group
				Calculated	Observed		
None	Orthorhombic $P2_12_12_1$	$a = 13.2 \text{ \AA}$ $b = 16.7$ $c = 5.2$	1159	1.31	1.3	4	—
1-Methyl (Barker, Emmerson & Periam, 1958)	Orthorhombic $P2_12_12_1$	$a = 15.2 \text{ \AA}$ $b = 11.6$ $c = 7.31$	1289	1.25	1.26	4	32.5
2-Methyl (Barker <i>et al.</i> , 1958)	Orthorhombic $P2_12_12_1$ or $P2_12_12$	$a = 16.9 \text{ \AA}$ $b = 14.6$ $c = 5.31$	1310	1.23	1.20	4	37.8
1,3-Dimethyl (Heaney & Lees, 1968)	Orthorhombic $Pbca$	$a = 22.4 \text{ \AA}$ $b = 17.5$ $c = 7.26$	2840	1.20	1.18	8	32.7
	Monoclinic $P2_1/c$	$a = 8.97 \text{ \AA}$ $b = 19.2$ $c = 8.16$ $\beta = 103^\circ$	1369	1.24	†	4	26.3
1,6,11-Trimethyl (Bartle <i>et al.</i> , 1965)	Monoclinic $P2_1/c$	$a = 16.9 \text{ \AA}$ $b = 7.41$ $c = 12.2$ $\beta = 98.4^\circ$	1515	1.19	1.19	4	29.7
1,3,6,11-Tetramethyl (Bartle <i>et al.</i> , 1965)	Monoclinic $P2_1/c$	$a = 8.53 \text{ \AA}$ $b = 22.4$ $c = 8.74$ $\beta = 105^\circ$	1613	1.17	1.17	4	28.4
2,3,6,7,10,11-Hexa- methyl (Heaney & Lees, 1968)	Monoclinic $P2_1/c$	$a = 8.42 \text{ \AA}$ $b = 20.8$ $c = 10.2$ $\beta = 100^\circ$	1747	1.19	1.20	4	26.8

* Accuracy estimated 1%.

† Not determined.

In general, X-ray photographs were recorded for several specimens about at least two crystallographic axes for each compound. For 2-methyltriphenylene, however, the thin acicular habit of the crystals allowed them to be mounted only about the c axis. Since precession photographs were too weak to confirm the presence or absence of odd 00/ reflexions, a space-group ambiguity remains for this compound. The monoclinic form of what is designated 1,3-dimethyltriphenylene was recognized in only one small specimen and it is possible that this was an isolated crystal of another dimethyltriphenylene.

Table 1 also includes a calculated volume per additional methyl group derived, by comparison with triphenylene itself, from the expression

$$v = n^{-1} [(V/Z) - (1159/4)] \text{ \AA}^3.$$

Here V is the cell volume of the substituted triphenylene and 1159 \AA^3 that of triphenylene; n is the degree of methyl-substitution; Z is the number of molecules per unit cell. Although there is a small tendency for V to decrease with

increasing substitution, its near constancy implies a remarkable similarity in efficiency of packing for these substituted triphenylenes.

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Refinement of the structure of magnesium thiosulphate hexahydrate, $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. By S. BAGGIO, L. M. AMZEL* and L. N. BECKA,* *Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*

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The structure of $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, determined by Nardelli, Fava & Giraldi (*Acta Cryst.* (1962), **15**, 225) has been refined with the use of more extensive data. The refinement by the full-matrix least-squares method with anisotropic temperature factors gives the dimensions of the thiosulphate ion as: S-S distance = 2.013 \AA , S-O distance = 1.468 \AA , O-S-O angle = 110.1°. Hydrogen atoms have been located in the three-dimensional difference Fourier synthesis.

The most accurate dimensions of the thiosulphate ion reported so far are those published by Nardelli *et al.* (1962) in their paper on the structure of $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. However, since the reported estimated standard deviations are too high to establish whether there is a significant change in dimensions of the thiosulphate moiety when it coordinates to a transition metal, we decided to refine that structure with more data. We also wanted to locate the positions of the hydrogen atoms to confirm the hydrogen bonding scheme predicted by Nardelli *et al.* (1962) and supported by the nuclear magnetic resonance studies of El Saffar (1968, 1969), the latter being in conflict with the n.m.r. results reported by Visweswaramurthy (1963).

The cell data are: $a = 9.397 \pm 0.010$, $b = 14.455 \pm 0.015$, $c = 6.864 \pm 0.009$ \AA ; $V = 932.4$ \AA^3 ; $D_c = 1.740$ ($Z = 4$), $D_o = 1.730$ g.cm $^{-3}$ (by flotation); $\mu = 7.0$ cm $^{-1}$ for Mo $K\alpha$ radiation; space group = $Pnma$. We determined the unit-cell dimensions from the $K\alpha_1$ - $K\alpha_2$ splitting of 89 independent high angle reflexions (recorded on levels $hk0$ to $hk5$ by the equi-inclination Weissenberg method with Cu $K\alpha$

radiation) by the least-squares procedure proposed by Alcock & Sheldrick (1967). Intensity data were collected with Zr-filtered Mo radiation on a cylinder shaped crystal of 0.9 mm length \times 0.25 mm diameter. Absorption corrections were neglected. We obtained 1589 independent reflexions of measurable intensity (70% of the reflexion sphere of $\sin \theta/\lambda = 0.90$) from mechanically integrated Weissenberg and precession photographs. The intensities were measured with a microdensitometer, and the different layers put on the same scale using the method of Hamilton, Rollett & Sparks (1965). The ratio of maximum observable intensity was 2500:1, and the discrepancy index ($R = \Sigma |I|/\Sigma F_o$) for equivalent reflexions measured on different layers is 0.06.

The observed and calculated structure factors are given in Table 1.

The final parameters for the non-hydrogen atoms were obtained by full-matrix least-squares refinement of the observed reflexions, minimizing $\Sigma w||F_o| - |F_c||^2$. The weights, w , are chosen to make $w\Delta^2$ approximately constant in the range of F_o and $\sin \theta/\lambda$. The form factors for S, O, Mg^{2+} and H are from *International Tables for X-ray Crystallography* (1962); the oxygen atoms of the $\text{S}_2\text{O}_3^{2-}$ ion were given a fractional charge of $-\frac{2}{3}$ each and their form factor was

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