LETTERS TO THE EDITORS

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Crystal Structure of Benzene : a New Type of Systematic Error in Precision X-Ray Crystal Analysis

LAST year, two of us gave a preliminary account[1] of an X-ray analysis of crystalline benzene from which a C—C bond-length of 1.37_8 A. was derived by differential syntheses with finite series corrections. We have since been able, by means of electronic computer programmes devised by Miss D. Pilling of this Department, to calculate Fourier maps and difference maps in the plane of the molecule, which clearly show that the thermal motion is markedly anisotropic, and detailed quantitative study shows that it is such as to produce a systematic error in the bond-length which is by no means negligible.

We have carried out, on the University of Manchester electronic computor, five cycles of refinement of the anisotropic thermal parameters of the carbon atoms, and find that the mean values of the components of the atomic temperature-factor B are :

Perpendicular to the plane of the ring	4.8×10^{-16} cm.^{2}
Radially in the plane of the ring	4.5×10^{-16} cm.^{2}
Tangentially in the plane of the ring	7.4×10^{-16} cm.^{2}

The difference of 2.9×10^{-16} between the last two figures shows, in agreement with nuclear resonance experiments[2], that an important part of the thermal motion of the benzene molecule at $-3°$ C. consists of rigid-body oscillations about its senary axis. Since the motion of an atom on an arc of a circle must produce a time-averaged electron distribution the maximum of which is displaced towards the centre of the arc, this oscillatory motion must cause the radius of the benzene ring, and therefore the C—C distance, to appear shorter than is actually the case. Displacements in the same sense, although probably smaller in magnitude, arise from oscillations about axes in the plane of the molecule. Detailed analyses of these effects indicate that the correction to the bond-length is at least 0·010 A. and is probably about 0·015 A. ; the corrected C—C bond-length derived from our work is about 1.39_2 A., which is now not significantly different from the value 1·397 A. obtained by Stoicheff[3]. Full details of our work will be submitted for publication shortly.

The computations involved in an anisotropic thermal motion analysis are very lengthy, and our work on benzene was only made possible by the availability of the University of Manchester computer. In most cases the corrections may well be too small to justify the computation which would be involved ; but it is clear that the possibility of systematic errors in atomic positions due to angular oscillations of the molecules (or of parts of them) arises in nearly all crystal structure analyses.

E. G. Cox
D. W. J. Cruickshank
J. A. S. Smith

Department of Inorganic and Structural Chemistry, University of Leeds. Feb. 26.

[1] Cox, E. G., and Smith, J. A. S., *Nature*, **173**, 75 (1954).
[2] Andrew, E. R., and Eades, R. G., *Proc. Roy. Soc.*, A, **218**, 537 (1953).
[3] Stoicheff, B. P., *Can. J. Phys.*, **32**, 339 (1954).

The Serpent Spring

IN the course of investigations concerned with the problem of obtaining large elongation or rotational effects by small variations of a force, the following peculiar behaviour of spiral springs has been observed.

A flat spiral spring, as an ordinary clock spring, is fixed at, for example, its inner end. At the outer end a force is applied in a direction perpendicular to the plane of the undeformed spiral. If this force is sufficiently strong, it deforms the spiral spring to a shape which resembles a lifting and uncoiling serpent, as will be seen if Fig. 1 is inverted. Therefore it may be called a 'serpent spring'. Such a spring is very sensitive, under certain conditions, to very small variations of the deforming force either in its magnitude or, in special circumstances, its direction. This sensitivity shows both in variations in length of the spring and in twist.

The sensitivity depends on the inclination of the acting force to the plane of the original spiral. At certain characteristic angles, for a definite magnitude of the acting force, the spring becomes extremely sensitive (critical region). The spring generally shows two different critical shapes. These depend upon the sense of inclination, for example, inclining the clamped end upwards (Fig. 1) or downwards. Fig. 1 has been obtained by photographing a spring in three different states on the same film, corresponding to equal steps in increasing weight. The spring is shown shortly before the critical state ; the shapes are reversible, that is, the spring returns to the same
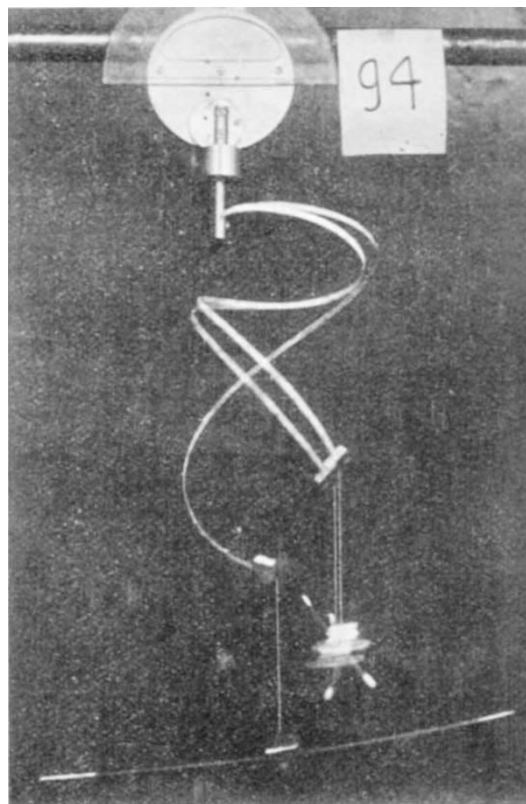

Fig. 1. Critical shapes of a serpent spring
Inclination $= +12.5°$. Spring steel, $a = 2.5$ mm., $b = 0.2$ mm. Original spiral : 1 turns ; outer diameter, 100 mm. ; inner diameter, 80 mm. Loads : 9·6 ; 10·1 ; 10·6 gm.