

## LETTERS TO THE EDITORS

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## Structure of Cyclo-octatetraene

We have been engaged in an investigation of the structure of cyclo-octatetraene by X-ray methods. In a previous communication<sup>1</sup>, we gave the preliminary crystallographic data. Cyclo-octatetraene crystallizes in the orthorhombic system with four molecules per unit cell. The cell dimensions are  $a = 7.76$  A.,  $b = 7.80$  A. and  $c = 10.66$  A. The space group is  $Aba$ .

The work has now been carried further to the point where the essentials of the structure are known, and accounts of the structure have been presented at several scientific conferences<sup>2,3,4</sup>.

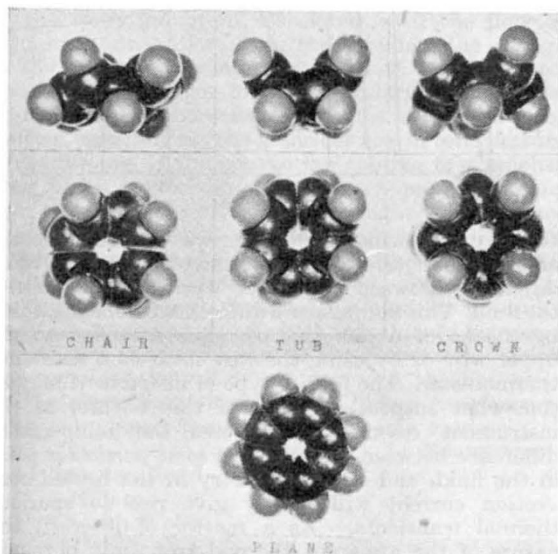


Fig. 1

Four structures can be postulated for the cyclo-octatetraene molecule (see Fig. 1): the 'crown' form—all *trans* configuration; the 'tub' form—all *cis*; the 'chair' form—half *cis*, half *trans*; and the 'plane' form, which presumes a large resonance energy to overcome the strain.

Raman and infra-red data obtained by Lord and Lippincott<sup>5</sup> led these investigators to favour the crown form. Similar experiments by Thompson<sup>6</sup> indicate the tub form to be most probable. Based on their recent electron diffraction study, Hassel<sup>7</sup> and

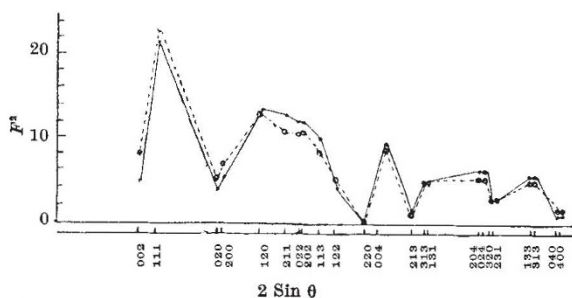


Fig. 2. COMPARISON OF OBSERVED (FULL LINE) AND CALCULATED (BROKEN LINE)  $F^2$  VALUES

co-workers conclude that the structure is the crown form with bond-lengths approximately those of benzene, suggesting a high degree of resonance.

Bragg-Lipson<sup>8</sup> structure factor charts proved very useful in our work. It was found that only the tub form with alternating single- and double-bonds gave a good fit with the experimental data (Fig. 2). The two-fold axis required by the space group must pass through the single bonds, and the bond-lengths are typically aliphatic: double-bond length, 1.34 A.; single-bond length, 1.54 A.; and C=C—C bond angle 125°. These values indicate little or no resonance energy in the cyclo-octatetraene molecule, which is in accord with the latest thermochemical data of Rossini<sup>9</sup> and co-workers.

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<sup>1</sup> Kaufman, Fankuchen and Mark, *J. Chem. Phys.*, **15**, 414 (1947).

<sup>2</sup> American Society for X-Ray and Electron Diffraction, Quebec (June 1947).

<sup>3</sup> 11th International Congress of Pure and Applied Chemistry, London (July 1947).

<sup>4</sup> American Chemical Society, New York (September 1947).

<sup>5</sup> Lippincott and Lord, *J. Amer. Chem. Soc.*, **68**, 1868 (1946).

<sup>6</sup> Lecture at the Polytechnic Institute of Brooklyn (March 8, 1947).

<sup>7</sup> Bastiansen, Hassel and Langseth, *Nature*, **160**, 128 (1947).

<sup>8</sup> Bragg and Lipson, *Z. Krist.*, **95**, 323 (1936).

<sup>9</sup> Prosen, Johnson and Rossini *J. Amer. Chem. Soc.*, **69**, 2068 (1947).

## Infra-Red Absorption Spectra of Crystals

SPECTROSCOPIC investigations on the scattering of light in crystals show very plainly that their vibration spectra have a discrete structure manifesting itself as a set of lines with sharply defined frequency shifts. That a similar discrete structure is also to be seen in the infra-red absorption spectra of crystals when examined under appropriate conditions is shown by a remarkable investigation by Barnes and Brattain<sup>1</sup>. These authors examined the case of magnesium oxide, which is a crystal of the cubic class with a structure similar to that of rock-salt. Plates obtained by cleavage from flawless transparent single crystals of large size were employed, and the absorption spectra of a whole series of such plates from the very thinnest obtainable to the thickest were investigated. The rock-salt spectrometer used in the study covered the wave-length range 1-15.6  $\mu$ , and the galvanometer deflexions were amplified 150 times by a photo-electric relay system. The resulting data showed the presence of some forty absorption lines in the wave-length range 6-15.5  $\mu$ . In the absorption curves reproduced with their paper, these lines are so sharply defined that their positions can be measured with high precision.

The theory of the vibration spectra of crystals worked out by me<sup>2</sup> leads to the result that crystals having the rock-salt structure have nine fundamental eigen-frequencies. These frequencies have now been evaluated theoretically, and their values for the case of magnesium oxide expressed as infra-red wave-lengths come out as 14.2, 14.7, 15.35, 17.1, 19.0, 21.1, 23.4, 38.5 and 54.5  $\mu$  respectively. All except the first three lie outside the range of a rock-salt spectrometer. Hence, except for the first three fundamentals, the absorption spectra recorded by Barnes and Brattain represent a superposition of the spectra of various orders higher than the first, in other words,