

used as a high-speed compact stroboscopic source, with a mean rating of 125 watts and a repetition frequency exceeding 160 flashes per second.

We are indebted to Mr. L. J. Davies, director of research, British Thomson-Houston Co., Ltd., Rugby, for permission to publish this letter.

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<sup>1</sup> Beeson, E. J. G., *Nature*, **134**, 453 (1949).

<sup>2</sup> Beeson, E. J. G., *Phot. J.*, **89B** (May-June 1949).

### Theoretical Determination of Electron Density in Organic Molecules

A RECENT communication under the above title<sup>1</sup> prompts us to put on record some recent results which we have obtained.

(1) One of us (N. H. M.<sup>2</sup>) has made detailed calculations of the actual electronic density in benzene at points in the molecular plane and in a parallel plane chosen to exhibit the influence of the  $\pi$ -electrons as much as possible. It appears that, except for certain small regions just above and below the carbon atoms, the contribution from the  $\sigma$ -electrons exceeds that from the  $\pi$ -electrons everywhere, and often by a large factor. It appears almost correct, therefore, to describe the  $\pi$ -electrons as imbedded in a denser 'sea' of  $\sigma$ -electrons. These calculations used both conventional molecular-orbital functions and a new solution of the Thomas-Fermi equation. Theoretical discussions of the density exclusively in terms of  $\pi$ -electrons, and without due recognition of the  $\sigma$ -electrons, are likely to lead to quite false conclusions. This is in keeping with recent work of Dr. S. L. Altmann<sup>3</sup> at King's College, who shows that  $\sigma$ - $\pi$  resonance is important even in the ground-state of aromatic molecules.

(2) Another of us (P. W. H.<sup>4</sup>) has studied the effect of molecular vibration on the peak densities likely to be recorded by X-ray analysis. The charge-cloud for a non-vibrating atom can be computed wave-mechanically. If we suppose, as a first approximation, that the atom carries this charge with it as it vibrates, then a 'smearing-out' occurs. The peak density in the vibrating molecule is drastically reduced below its value in the non-vibrating molecule. Thus it is highly dangerous to compare the observed (that is, vibrating) density with that calculated (usually non-vibrating). This is also true, though in a reduced manner, for the bridge values of the density in the centres of the various C-C bonds. In addition to this, X-ray measurements are made on a crystal, and it appears that translation and libration of the molecule as a whole significantly change the density distribution in each unit cell. Theoretical analysis of the observed distribution shows that these latter motions are much more important than the internal vibrations in affecting the charge density.

(3) In conclusion, it seems desirable to point out that present X-ray observations, such as those of Abrahams, Robertson and White<sup>5</sup>, give the density only at points in the molecular plane. Here, on account of their nodal plane, the  $\pi$ -electrons contribute nothing at all to the density except as a result of fairly large molecular vibrations. It appears from Dr. Klement's letter<sup>1</sup> that he has studied

only the  $\pi$ -electrons. If that be so, then what he calls the exchange density in a bond may be shown to be closely related to the conventional  $\pi$ -bond order. Direct check with observation (other than with bond-lengths<sup>6</sup>) cannot be made until Prof. J. M. Robertson uses his X-ray measurements to calculate the density in a parallel plane. Even then, as shown above, the  $\pi$ -electron distribution will be confused by that from the  $\sigma$ -electrons.

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<sup>1</sup> Klement, O., *Nature*, **168**, 162 (1951).

<sup>2</sup> *Acta Cryst.* (in the press).

<sup>3</sup> *Proc. Roy. Soc., A* (in the press).

<sup>4</sup> To be published.

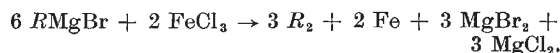
<sup>5</sup> *Acta Cryst.*, **2**, 238 (1949).

<sup>6</sup> Coulson, C. A., Daudel, R., and Robertson, J. M., *Proc. Roy. Soc., A*, **207**, 306 (1951).

### A New Type of Organo-Iron Compound

NUMEROUS investigators have studied the reaction of Grignard reagents with anhydrous ferric chloride, but have failed to isolate any organo-iron compounds or to produce any definite evidence for their formation in such reactions.

The statements by Job and Reich<sup>1</sup> and by Champetier<sup>2</sup>, that they have obtained stable ethereal solutions of compounds of the type  $RFeI$  by reaction of ferrous iodide with organo-zinc halides, are based solely on the formation of ferrous hydroxide on hydrolysis, and may be accounted for by the difference in solubility between ferrous and zinc hydroxides. Indeed, the evidence of Champetier's own experiments with Grignard reagents<sup>2</sup> suggests that such intermediates may be formed at low temperature, but are quite unstable above  $-40^{\circ}C$ . The normal reaction leads to reduction of the ferric salt and, with excess Grignard reagent, results in the formation of metallic iron according to the equation:



This reaction is of preparative value and has been shown to yield diphenyl from phenylmagnesium bromide in almost quantitative yield<sup>3</sup>.

As a possible route to 'fulvalene'<sup>4</sup>, we attempted to apply this reaction to cyclopentadienylmagnesium bromide. To a solution of this Grignard reagent (from 18 gm. ethyl bromide and 4 gm. magnesium in benzene with 11 gm. cyclopentadiene) was added an equivalent amount (9.05 gm.) of ferric chloride dissolved in anhydrous ether. After allowing the mixture to stand at room temperature overnight, it was refluxed (1 hr.) to ensure complete reaction, cooled and decomposed with ice-cold ammonium chloride solution in the usual manner. Evaporation of the dried organic layer yielded an orange solid (3.5 gm.). This was moderately soluble in ether, readily soluble in benzene and crystallized from methanol in large needles of melting point  $173-174^{\circ}C$ . (found: C, 64.6; H, 5.6; Fe, 30.1 per cent; molecular weight, by cryoscopic determination in benzene, 186.5.  $C_{10}H_{10}Fe$  requires: C, 64.6; H, 5.4; Fe, 30.0 per cent; molecular weight, 186.0). Iron was determined gravimetrically as  $Fe_2O_3$  after