Hemi-Dewar Biphenyl

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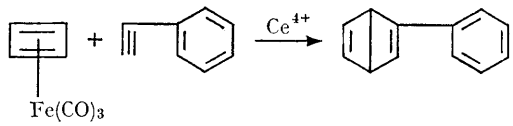
THE system (I) is of interest in that it represents a compound possessing two of the several renowned classical representations of a benzene nucleus incorporated as distinct entities within the same molecule. As one hundred years have now elapsed since the Kekulé structure for benzene was first proposed,[1] it is appropriate to report at this time the synthesis of this member of a family of several such possible systems.

Compound (I), which is referred to as hemi-Dewar biphenyl,[2] has now been prepared by decomposition of cyclobutadieneiron tricarbonyl (II) with ceric ammonium nitrate in the presence of phenylacetylene.[4] In the course of the oxidative decomposition of the complex a molecule of cyclobutadiene is transferred from (II) to phenylacetylene with the formation of hemi-Dewar biphenyl, (I). The product, which is purified by liquid chromatography over silica gel, is obtained as a colourless oil (n_D^{26}, 1·5834).



(II) (I)

The principal evidence for the assignment of structure (I) to the compound is seen in the n.m.r. spectrum. (Figure 1) The areas of the absorption bands centred at τ 2·80, 3·43, 6·00, and 6·20 occur in the ratio 5 : 3 : 1 : 1 respectively; these are readily assigned in the order given, to the five aromatic, three olefinic, and the two non-equivalent allylic hydrogens expected for structure (I).

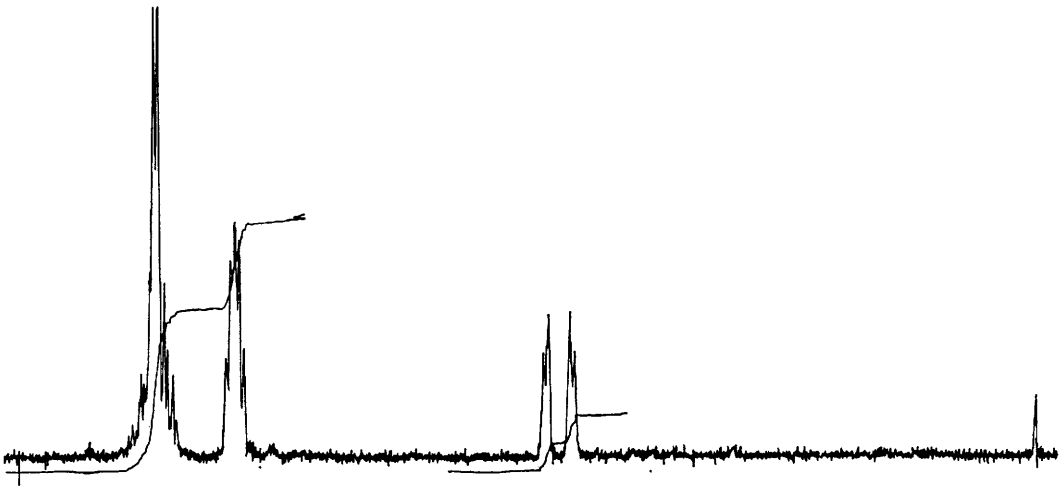


FIGURE 1. *N.m.r. Spectrum of Hemi-Dewar Biphenyl.*

In addition the ultraviolet absorption spectrum of the material resembles that of styrene; also the infrared absorption spectrum shows a sharp absorption at 1555 cm.$^{-1}$ expected for a cyclobutene derivative.[5] Finally, upon heating to 90° for several minutes the material is converted quantitatively into biphenyl.

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[1] A. Kekulé, *Bull. Soc. chim. France*, 1865, **1**, 98.
[2] The prefix "Dewar" remains a very convenient term to indicate the bicyclo[2,2,0]hexadiene skeleton; it being clear that this system, because of its particular stereochemistry, is not the familiar Dewar canonical form used in valence-bond parlance and due cognizance being taken of the intentions of Professor Dewar in introducing this structure to the literature (ref. 3).
[3] see W. Baker, *Chem. in Britain*, 1965, **1**, 191.
[4] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.
[5] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, 1961, **83**, 1226.