lowest metastable state the defect is spread : one shared electron enters the π-orbital (though there is room for two), while three unshared electrons occupy the non-bonding orbitals (where there is room for four). The CC bond is thus a three-electron bond. Hence it can be understood that, while the angle is the same as in either normal ethylene or benzene (120°), the lengths are practically identical with those in benzene (usually given as CC = 1·39 A., CH = 1·08 A.), and the force-constants markedly resemble those of benzene (recorded[1] as $F = 7\cdot6 \times 10^5$ dyne/cm., $\delta = 8\cdot0 \times 10^{-12}$ dyne-cm./radian).

This first precise elucidation of a marked change of molecular shape on electronic excitation may be indicative of a common phenomenon in excitations of simple π-electron systems[2].

Some of the weaker bands were measured with a multiple reflexion cell kindly lent by Dr. W. C. Price. The analysis was aided by discussions with Prof. R. Mecke and Dr. G. Herzberg, and by many with Prof. D. P. Craig. We thank these friends for their help.

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Polarization of the Second Ultra-violet System in Hexamethylbenzene

ALLOWED electronic transitions in aromatic molecules between states approximately described by combinations of $p\pi$ atomic orbitals must all be polarized in the molecular plane, and the same is true of the much weaker transitions which take on allowed character only because of the disturbing effect of nuclear vibrations. This is the polarization property actually found in band systems so far studied experimentally, almost all of which have been lowest-energy transitions. Specifically, Scheibe[1] showed that the 2800-A. system of hexamethylbenzene is polarized with the active electric vector in the molecular plane. This system certainly corresponds to the well-known 2600 A. system of benzene itself, which is assigned $A_{1g} - B_{2u}$ from vibrational analysis. Hexamethylbenzene crystallizes with all the molecular planes parallel to one another, and perpendicular to the main faces of a sublimed crystal, and so is much better suited to polarization measurements than benzene.

In the upward sequence of excited states, corresponding to band systems at higher energies and shorter wave-lengths, it is to be expected that new types of atomic orbitals will be needed in the approximate molecular wave functions. Thus atomic ns and np orbitals are required in the upper states of the vacuum ultra-violet transitions studied in benzene by Price and Wood[2] ; and in discussing the question which of the observed band systems is the lowest in which s atomic orbits participate, Hammond, Price, Teegan and Walsh[3], affirming in more specific terms an assignment made earlier by Carr and Stücklen[4], proposed that the second benzene system,

that at 2000 A., was the lowest such Rydberg transition, implying that its polarization is perpendicular, and not parallel, to the molecular plane.

We have now studied the polarization of the 2300-A. system of hexamethylbenzene, which corresponds to the 2000-A. system in benzene, and find that the electric vector lies in the molecular plane, just as in the long wave-length system. Measurements of the extinction ratio in the two polarizations show that absorption perpendicular to the molecular plane, while not necessarily zero, is less than ten per cent of that in the plane. Applied to benzene, these results indicate that the 2000-A. system is polarized predominantly in the molecular plane. It remains possible that the first ns Rydberg band system underlies the 2000-A. absorption, even though this does not appear to be true in hexamethylbenzene, but is very much weaker than hitherto supposed ; alternatively, it may fall elsewhere in the spectrum. Polarization in the molecular plane is, however, consistent with the assignment of the upper state of this system to a π-electron state, whether this be the B_{1u} state as originally suggested by Goeppert-Mayer and Sklar[5] or the E_{2g} state as proposed more recently by one of us[6].

The polarization measurements were made with a Hilger medium quartz spectrograph. A selected calcite rhomb, transparent to 2150 A., was mounted immediately behind the slit and the crystal of hexamethylbenzene (a sublimation flake between silica disks) placed before it on a rotating stage. Each exposure gave two adjacent images, corresponding to two directions of plane-polarization. One such exposure is shown in the accompanying photograph.

2400 A.   2200 A.

Hexamethylbenzene photographed through a calcite rhomb. The upper beam is polarized in the molecular plane, the lower perpendicular to it

Comparison of the two images from a single exposure gives an immediate though rough indication of polarization properties ; but to avoid discrimination within the spectrograph and for other reasons, we actually used one beam at a time, rotating the crystal between exposures and comparing the results with the crystal structure[7] interpreted by a study of the same crystal with the polarizing microscope.

This work will be published more fully, with a discussion of its theoretical implications. We thank Dr. P. G. Owston for important aid in microscopy, and for many helpful discussions.

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