# SPECTROSCOPIC PROPERTIES OF KEKULENE

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Kekulene [1,2] is the first example of a new class of aromatic compounds in which the annelation of six membered rings leads to a cyclic system enclosing a cavity with hydrogen atoms (see fig. 1). On the basis of the X-ray structure analysis [2] kekulene has $D_{6h}$ symmetry and seems to be built up by phenanthrene-like subunits. Fluorescence from the first excited singlet state ($^1B_{2u}$) and phosphorescence from the lowest excited triplet state ($^3B_{1u}$) should therefore be symmetry forbidden. Nevertheless, both emissions are observed due to a reduction of symmetry in the host matrix. Fig. 2 shows the fluorescence (F) and phosphorescence (P) of kekulene (concentration $< 10^{-6}$m) in tetrachlorobenzene at 1.3 K. The excitation of the polycrystalline sample occured due to direct singlet-triplet absorption of the host matrix followed by energy transfer to the kekulene molecules. This excitation results at 1.3 K in some weak additional P from tetrachlorobenzene X-traps at higher energies. The emission spectrum of kekulene is composed of F and P from two different sites (I and II) with 0.0-bands at 22082.4 cm$^{-1}$(I) and 21978.0 cm$^{-1}$(II) for F and 17073.3 cm$^{-1}$(I) and 16985.9 cm$^{-1}$(II) for P. For both sites the same low energy skeleton vibrations are observed within the error limit (250, 443, 685, 745, 969 and 1239 $\pm$ 5 cm$^{-1}$ in F and 1279, 1297, 1420 and 1618 $\pm$ 5 cm$^{-1}$ in P). The triplet zero field splitting parameters $|D|$ and $|E|$ of both traps were measured by optical detection of magnetic resonance (ODMR) in zero field. For site I values of $|D| = 0.10622$ cm$^{-1}$ and $|E| = 0.001935$ cm$^{-1}$ and for site II $|D| = 0.10533$ cm$^{-1}$ and $|E| = 0.00362$ cm$^{-1}$ were found. From the fact that the E values

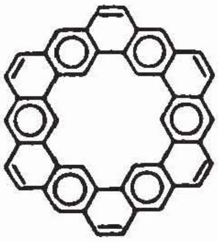

Fig. 1
Kekulene

are found to be non-vanishing it follows that the symmetry of kekulene in its phosphorescent state is lowered in the tetrachlorobenzene matrix and the molecule no longer possesses the six-fold symmetry axis. However, the E value is still very small as expected and for kekulene in tetrabromobenzene $|E| = 0.00074\ cm^{-1}$ ($|D| = 0.10378\ cm^{-1}$) is the smallest E-parameter observed so far in triplet states of aromatic molecules.

For site I molecules kekulene is believed to remain planar because only one zero field spin level is observed to be radiative in the 0.0-band as expected for a planar molecule. Hence the molecule is assumed to be distorted to a quinoidal or antiquinoidale form. In contrast, site II kekulene molecules might have some out of plane distortion because two zero field spin levels are strongly radiative in the 0.0-band.

The measured D parameters foı kekulene are relatively large and very similar to those of phenanthrene ($|D| = 0.1053\ cm^{-1}$, $|E| = 0.0468\ cm^{-1}$ in PMMA [3]). On the other hand, the value of $|D| = 0.101\ cm^{-1}$ calculated within a semiempirical π-theory [4] for kekulene agrees well with those experimentally obtained.

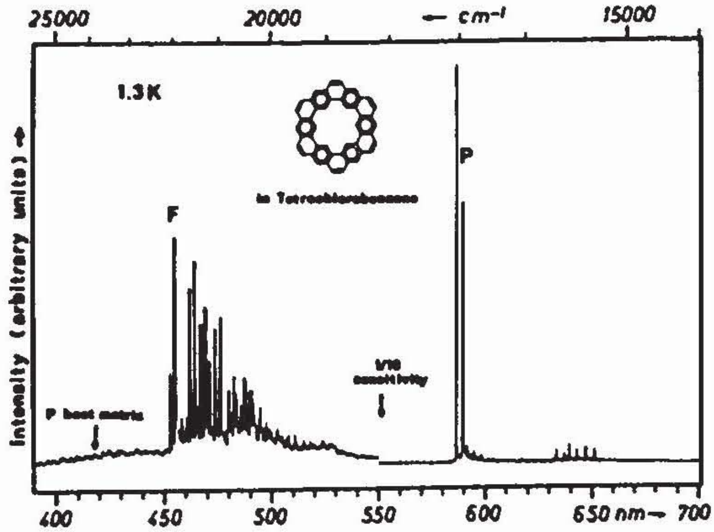

Fig. 2

Fluorescence (F) and phosphorescence (P) of kekulene in tetrachlorobenzene at 1.3 K

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