Electronic properties of kekulene†

by D. SCHWEITZER and K. H. HAUSSER

Abt. Molekulare Physik, Max-Planck-Institut, Jahn-Straße 29,
6900 Heidelberg, Germany

and H. VOGLER, F. DIEDERICH and H. A. STAAB

Abt. Organische Chemie, Max-Planck-Institut, Jahn-Straße 29,
6900 Heidelberg, Germany

The fluorescence and phosphorescence of kekulene in a host matrix of polycrystalline tetrachlorobenzene are investigated, together with the triplet zero field splitting parameters $|D|$ and $|E|$ obtained by ODMR in zero field. The D value is also calculated within a semi-empirical π-theory and compared with experiment. It could be shown that the triplet state energies of a number of different sites of kekulene in the host matrix and the zero field splitting parameters are related, in first order, by spin orbit interaction.

1. INTRODUCTION

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 lined with hydrogen atoms (figure 1). On the basis of the X-ray structure analysis [2] the sextet notation for kekulene shown in figure 1 is undoubtedly the best representation of the actual bonding situation out of the 200 possible structures with different arrangements of double and single bonds which can be formulated [3]. The X-ray structure analysis has further shown that kekulene has an almost perfect planar structure in the ground state (the maximum deviation of carbon atoms from the mean plane through the 48 carbon atoms is only 7 pm). Therefore kekulene has D_{6h} symmetry and seems to be built up by phenanthrene like subunits.

Because of the D_{6h} symmetry, fluorescence from the first excited singlet state ($^1B_{2u}$) and phosphorescence from the lowest excited triplet state ($^3B_{1u}$) should be symmetry forbidden. Nevertheless, both emissions are observed from kekulene in the host matrix due to a reduction of symmetry. This behaviour is similar to that observed for coronene in n-alkane matrices [4, 5], where the so-called Shpol'skii effect [6] is intensive. Because the solubility of kekulene is very poor, it was not possible to use such n-alkane crystals or polycrystals, but instead polycrystalline 1,2,4,5-tetrachlorobenzene or 1,2,4,5-tetrabromobenzene matrices were used as hosts. The kekulene concentration

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in these matrices was 10^{-6} M or smaller. Besides the fluorescence and phosphorescence emissions it was possible to observe the triplet zero-field splitting parameters, D and E, by optical detection of magnetic resonance (ODMR), and these are compared with those calculated within a semi-empirical π-theory and discussed in terms of contributions of different substructures of the molecule.
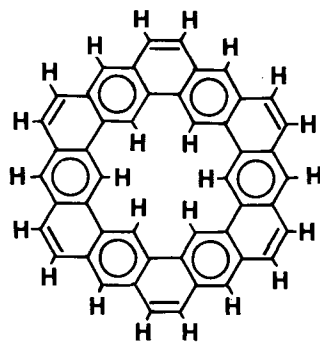

Figure 1. The structure of the kekulene molecule.

2. EXPERIMENTAL

Purified kekulene [1, 2] was dissolved in zone-refined liquid 1,2,4,5-tetrachlorobenzene or 1,2,4,5-tetrabromobenzene. Polycrystalline samples were prepared by rapidly cooling the liquid samples and by tempering them at room temperature for several weeks. The samples were placed into a liquid helium cryostat and the temperature reduced to 1·3 K by pumping. Optical excitation was performed with a HBO 200 mercury lamp in combination with a Shoeffel GM 250 monochromator and Schott UV-R-340 and UG 11 filters, or by an argon ion laser (Coherent CR 6 UV) and an additional interference filter. The excitation of the polycrystalline samples occurred due to a direct singlet triplet absorption of the host matrices followed by energy transfer to the kekulene molecules. In both solvents the lowest triplet states of the host matrices are energetically (at least 2500 cm^{-1}) higher than the first excited singlet states of kekulene. The advantage of this mode of excitation was that the whole sample was excited so that an intense fluorescence and phosphorescence from kekulene could be observed. A direct excitation of the kekulene molecules by singlet singlet absorption (420–440 nm, Hg-lamp) resulted in a very weak emission due to the weak absorption of the symmetry-forbidden $S_0(^1A_{1g}) - S_1(^1B_{2u})$ transition. The fluorescence and phosphorescence was monitored at right angles to the excitation path with a Spex 1402 (0·85 m) double monochromator equipped with a cooled ($-50°$C) RCA 31034 A02 photomultiplier in combination with a photon counting system (PAR 1109). The ODMR apparatus was essentially the same as described earlier [7]. Signal averaging was employed by using a transient recorder (Biomation 8100) and an additional computer system (Dietz 621, 48 K).

3. RESULTS

Figure 2 (*a*) shows the fluorescence (F) and phosphorescence (P) of kekulene in 1,2,4,5-tetrachlorobenzene at room temperature, while figure 2 (*b*) shows both
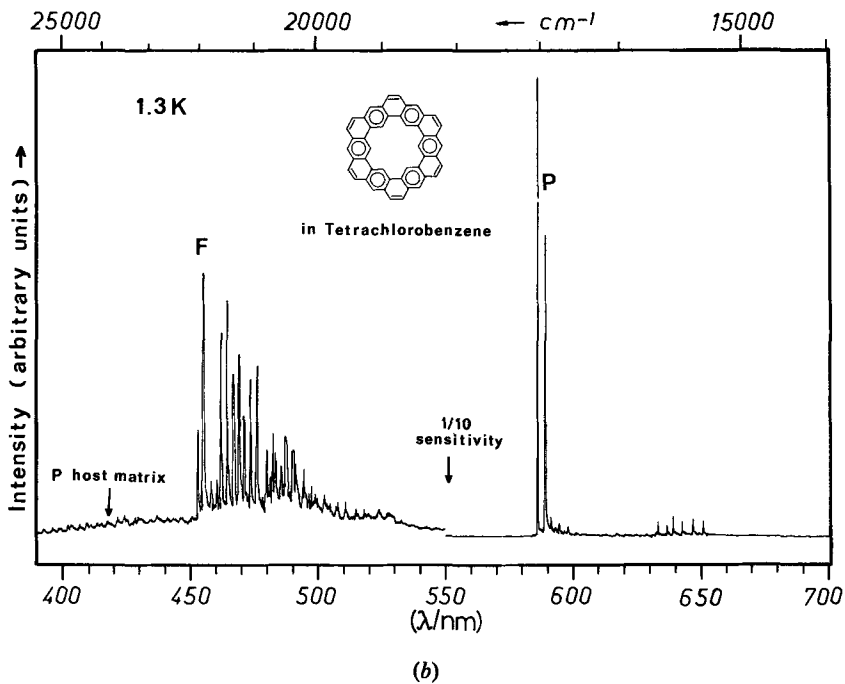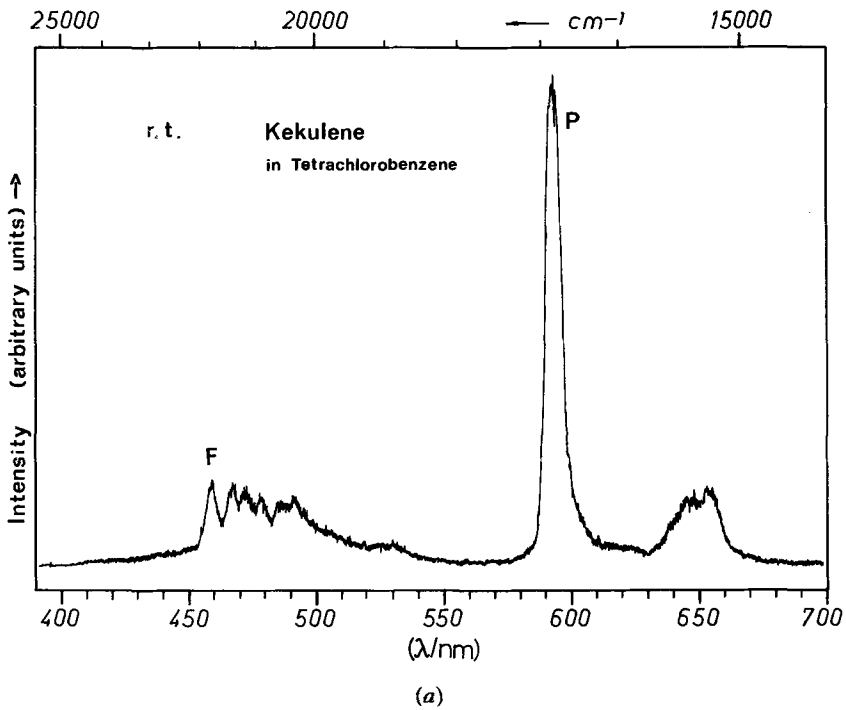
Figure 2. Fluorescence (F) and Phosphorescence (P) of kekulene in 1,2,4,5-tetrachloro-
benzene (*a*) at room temperature, (*b*) at 1·3 K. The phosphorescence (P) of
kekulene at 1·3 K was recorded with a spectrometer sensitivity 0·1 × that used to
observe the fluorescence. Emissions at room temperature and at 1·3 K were
taken with identical resolution conditions.

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emissions at 1·3 K under the same experimental conditions. The excitation due to the singlet–triplet absorption of the host matrix results, at 1·3 K, in some weak additional phosphorescence from tetrachlorobenzene x-traps at higher energies. The phosphorescence (P) of kekulene at 1·3 K was taken with 1/10 the sensitivity used for recording the fluorescence. The relatively strong emission from the lowest triplet state of kekulene is due to an intermolecular heavy atom effect of the chlorine atoms of the host matrix tetrachlorobenzene.

The emission spectrum of the tempered samples at 1·3 K (figure 2 (*b*)) is composed of fluorescence and phosphorescence from two different sites (I and II) with 0–0 bands as shown in table 1. Untempered samples show emission from additional sites. Figure 3 (*a*) shows the fluorescence of a tempered sample at 1·3 K under higher resolution. The emissions from sites I and II are labelled by × and ○, respectively. The phosphorescence obtained under the same experimental conditions is shown at the bottom of figure 3 (*b*). The emission from the two different sites I (×) and II (○) was discriminated by ODMR measurements in zero field. In addition, for both sites, the same low-energy skeleton vibrations are observed within the error limit, i.e. 250, 443, 685, 745, 969 and 1239 ± 5 cm^{-1} for fluorescence and 1279, 1297, 1420 and 1618 ± 5 cm^{-1} for phosphorescence. It was further assumed that site (I), with the higher energy in the phosphorescence, possesses also the higher energy in the fluorescence emission.

Table 1. Data relating to the 0–0 bands of the fluorescence and phosphorescence from several sites of kekulene in 1,2,4,5-tetrachlorobenzene at 1·3 K, together with the corresponding triplet zero-field splitting parameters $|D|$ and $|E|$ as measured by ODMR in zero field.

	0–0 bands		Zero field splitting parameters	
Site	S_1 (cm^{-1})	T_1 (cm^{-1})	$|D|$ (cm^{-1})	$|E|$ (cm^{-1})
	—	17117·4	—	—
	—	17093·3	0·10613	0·00164
	—	17079·2	0·10619	0·00174
I (×)	22082·4·	17073·3	0·10622	0·00194
	22024·3†	17024·9	0·10569	0·00211
		16990·2	0·10504	0·00321
II (○)	21978·0	16985·9	0·10533	0·00362
		16911·9	0·10371	0·00489

† This is the most intense additional band of some very weak new bands which appear in the fluorescence spectrum of kekulene in tetrachlorobenzene after 12 hours of irradiation with U.V. light (see figure 5 for the phosphorescence).

The triplet zero-field splitting parameters, $|D|$ and $|E|$, (measured by ODMR in zero field) for sites I and II and a number of other sites, which will be explained later, are given in table 1.
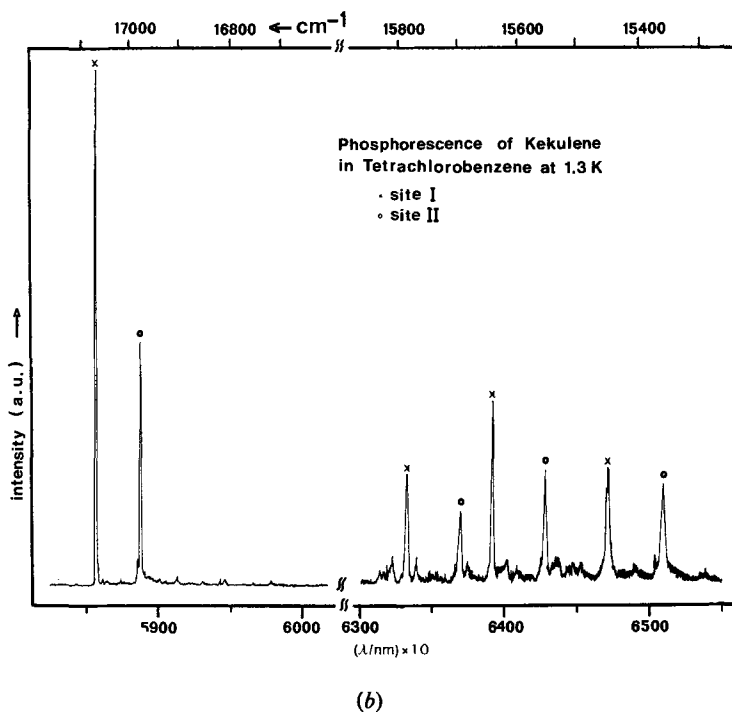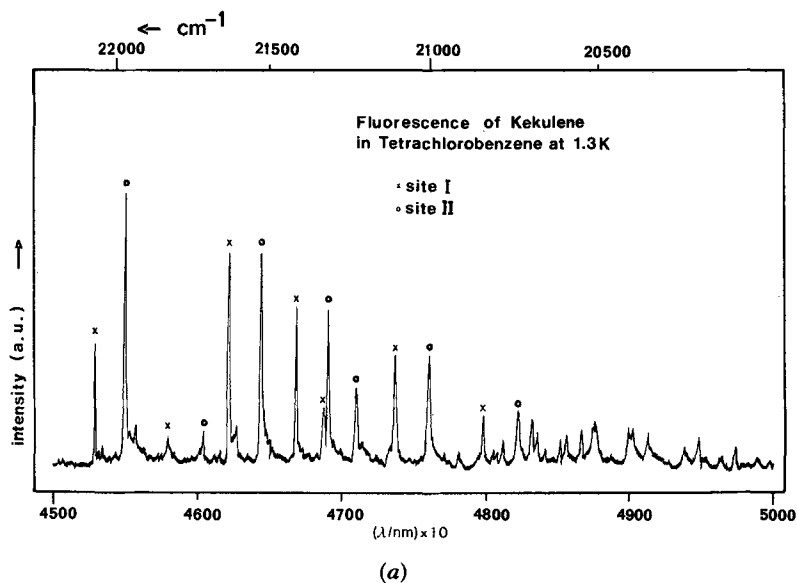
(a)

(b)

Figure 3. (a) Fluorescence of sites I (×) and II (○) of a tempered kekulene sample (in tetrachlorobenzene) at 1·3 K under high resolution. (b) Phosphorescence of the same sample.

Figure 4 (a) shows the slow passage signal of the $|D| + |E|$ transition monitored, for site I, on the 0–0 band. The half width of 2·1 MHz is relatively small for a polycrystalline sample. While the $2|E|$-transition at 116·1 MHz

was nearly as intense as the $|D| + |E|$-transition, the $|D| - |E|$-transition could only be observed under double resonance conditions, i.e., additional continuous irradiation with microwaves of the frequency of the $2|E|$ or $|D| + |E|$-transition. This means that, for site I, only one in-plane triplet sublevel is radiative (top level). For site II, all three transitions (217·2 MHz, 3·051 GHz, 3·2685 GHz) could be observed under slow passage conditions corresponding to at least two radiative triplet sublevels.
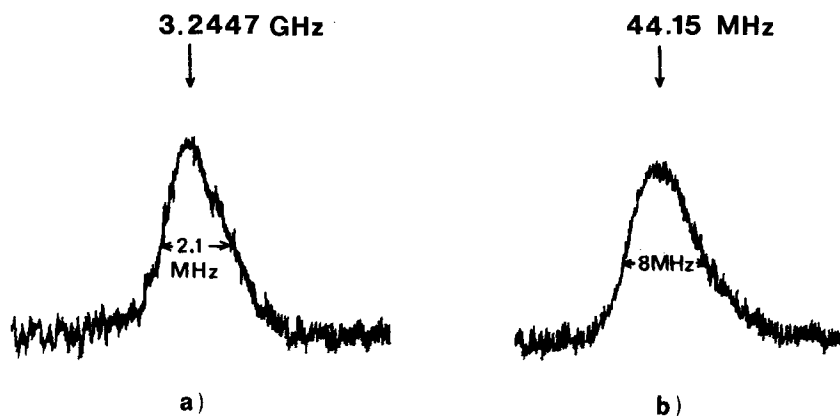

Figure 4. (a) Slow passage ODMR signal of the $|D| + |E|$ transition of kekulene in 1,2,4,5-tetrachlorobenzene at 1·3 K for site I monitored on the 0–0 band at 17 073·3 cm^{-1}. (b) Slow passage ODMR signal of the $2|E|$ transition of kekulene in 1,2,4,5-tetrabromobenzene at 1·3 K and 16 886·1 cm^{-1}.

The dynamic parameters of kekulene are affected by an intermolecular heavy atom effect arising from the chlorine atoms of the host matrix. The measured average decay rate $\rho = 1/3(k_x + k_y + k_z)$ for site I was 0·58 sec^{-1}. This decay rate ρ was observed, after turning off the light with an electronic shutter, under simultaneous continuous irradiation of the two microwave frequencies corresponding to the $2|E|$ and $|D| + |E|$-transitions.

Under the same conditions, but without microwave power, a single exponential decay with a rate of 0·43 sec^{-1} was observed. MIDP experiments [8] did not give signals because strong spin lattice relaxation rates between the triplet sublevels exist. This can be seen from the fact that, at 1·3 K, the decay rate of the fast passage signal [9], under continuous irradiation of light is a factor of 2·3 larger for the $2|E|$-transition than for the $|D| + |E|$-transition (0·58 sec^{-1} for the $|D| + |E|$-transition and 1·35 sec^{-1} for the $2|E|$-transition).

Figure 5 (a) shows the region of the 0–0-bands of the phosphorescence of site I and II for a fresh, tempered sample of kekulene in tetrachlorobenzene. In figure 5 (b) the phosphorescence emission is shown of the same sample after 12 hours of irradiation with U.V.-light of wavelengths between 3510 and 3610 A (~ 5 mW Argon-Ion-laser). The intensity of the phosphorescence of sites I and II is reduced by this irradiation and additional phosphorescence peaks appear which are due to new sites for kekulene molecules in the tetrachlorobenzene matrix and not due to photochemical products. This can be proved by a series of ODMR experiments in which the monochromator wavelength is changed after each experiment for selecting another emission peak.
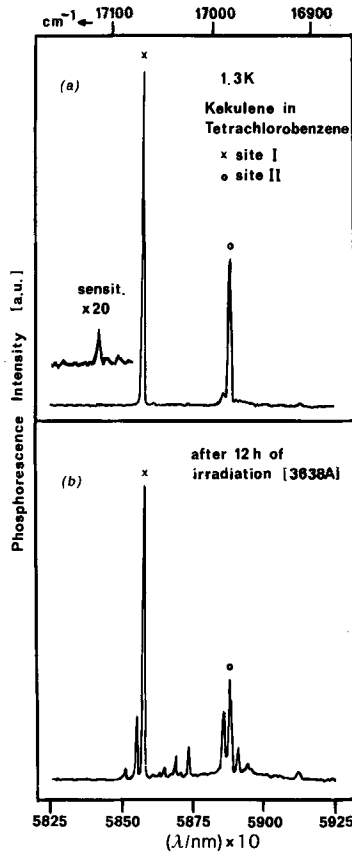
Figure 5. (*a*) Region of the 0–0 bands of the phosphorescence of site I (×) and II (○)
for a fresh, tempered sample of kekulene in tetrachlorobenzene. With higher
sensitivity of the spectrometer (× 20) a weak (w) phosphorescence peak at
17 117·4 cm^{-1} is observed (see text). (*b*) Same phosphorescence region as in (*a*)
of the same sample after 12 hours of irradiation with U.V. light (see text).

Table 1 shows the triplet zero-field splitting parameters $|D|$ and $|E|$ of seven
sites (including sites I and II) together with their $S_0 - T_1$ energy differences.
In figure 6 the zero-field splitting parameters $|D|$ and $|E|$ are plotted with
respect to these $S_0 - T_1$ energy differences.

No fluorescence could be observed for kekulene in 1,2,4,5-tetrabromo-
benzene. The strong phosphorescence emission is not as simple to interpret
as in the tetrachlorobenzene matrix because about 15 different sites are ob-
served. Table 2 shows the triplet zero-field splitting parameters $|D|$ and $|E|$
for the two prominent sites. For both sites, all three ODMR signals could be
observed by slow passage experiments, corresponding to the fact that at least
two triplet sublevels are radiative. Figure 4 (*b*) shows the $2|E|$-transition of
kekulene in tetrabromobenzene observed at the site with the highest phos-
phorescence intensity in the 0–0 band (16 886·1 cm^{-1}). The half width in this
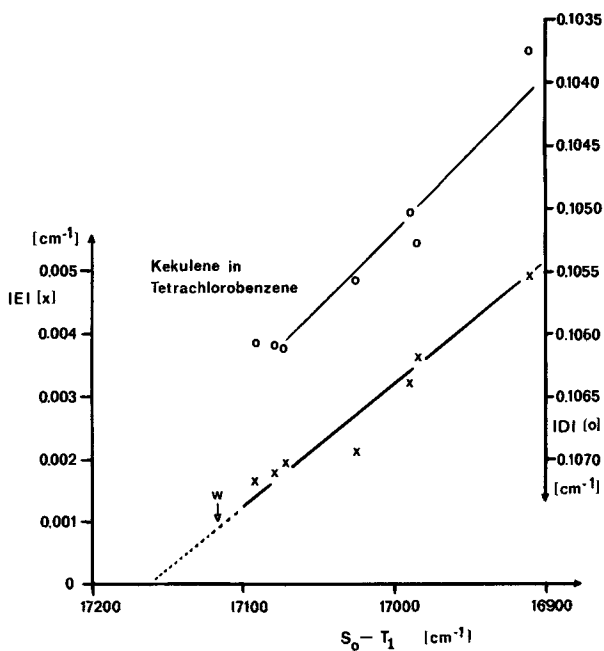case is 8 MHz, about a factor of 4 larger than in the case of tetrachlorobenzene.

Figure 6.   Zero field splitting parameters $|D|$ ($\bigcirc$) and $|E|$ ($\times$) as a function of the $S_0 - T_1$ energy differences of the corresponding sites (see table 1).

Table 2.   Data relating to the 0–0 bands of the phosphorescence and triplet zero-field splitting parameters $|D|$ and $|E|$ for the two prominent sites of kekulene in 1,2,4,5-tetrabromobenzene at 1·3 K.

0–0 band phosphorescence (cm^{-1})	$|D|$ (cm^{-1})	$|E|$ (cm^{-1})
17123·1	0·1039	0·0026
16866·1	0·1038	0·00074

4. Discussion

For both the fluorescence and phosphorescence of kekulene in tetrachlorobenzene, 0–0 bands are observed which are surprisingly strong, considering the fact that they are both spin- and symmetry-forbidden.   This spin-forbidden character is changed by the external heavy atom effect, which is well known to affect radiative processes in particular [10].

The symmetry conditions in kekulene require a more detailed discussion. When a molecule with a sixfold symmetry axis is placed into a crystalline environment of lower symmetry, its first excited singlet and triplet states might no longer possess a sixfold symmetry axis.   From the comparatively small E-values observed, we must conclude that the distortion is not very large.   The two main sites (I and II) behave somewhat differently.   For site I, the 0–0 band phosphorescence occurs from one of the triplet sublevels only.   This behaviour can be explained by distortion to a quinoidal or antiquinoidal form,

similar to coronene in n-alkane matrices [4, 5], although the strength of the emission is somewhat surprising in view of the small E-value. The kekulene molecules in site II, on the other hand, radiate strongly from at least two triplet sublevels and somewhat less strongly from the third level, but we do not know quantitatively the strength of the radiation from this third level. The strong radiation from two triplet sublevels could originate from an intermediate form as described for benzene [11]. The fact that the third level is radiative as well, however, seems to indicate some out of plane distortions.

Considering the size of the molecule the measured D-parameter of kekulene is surprisingly large and very similar to that of phenanthrene ($D = 0.1053$ cm^{-1}, $E = 0.0468$ cm^{-1} in PMMA [12]). Therefore a calculation of the D-value of kekulene was carried out within a semi-empirical π-theory [13] which has been successfully applied to a large number of benzenoid hydrocarbons. With these compounds the use of an idealized geometry with a fixed standard bond-length, i.e., $r_{01} = 1.397$ Å was a sufficient approximation since the bond orders in the lowest triplet states varied considerably less than those of the ground state. Assuming a linear relationship [14] between bond orders, P_{st}, of the corresponding state and bond lengths, r_{st}, for bonded atoms s and t, i.e. $r_{st} = A + BP_{st}$, it follows that the bond lengths in the lowest triplet state should be more uniform than in the ground state. In the case of kekulene, however, the use of a fixed bond length is not a sufficient approximation for the lowest triplet state since it results in a too small value $D = 0.089$ cm^{-1} [15].

Taking the parameters $A = 1.572$ Å and $B = -0.274$ Å and applying the relationship [14] $\beta_{st}/\text{eV} = C \exp\left(-2.411\, r_{st}/\text{Å}\right)$ between bond lengths r_{st} and resonance integrals β_{st} between bonded atoms s and t, where C was chosen in

Table 3. Experimental and calculated bondlengths of kekulene in the ground state ($^1r_{st}$) and lowest triplet state ($^3r_{st}$).

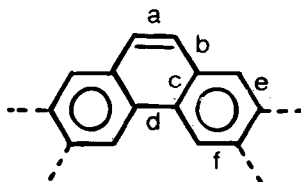| Bond†	$^1r_{st}$ (calc.)/Å	$^1r_{st}$ (exp.)/Å[2]‡	$^3r_{st}$ (calc.)/Å
a	1·346	1·347	1·359
b	1·449	1·444	1·444
c	1·423	1·425	1·429
d	1·458	1·459	1·456
e	1·402	1·398	1·408
f	1·400	1·388	1·404

† See figure 7.
‡ Averaged values.

Figure 7. Labelling of the chemical bonds in kekulene used in table 3.

order to reproduce the standard resonance integral [13], we obtain bond lengths (self-consistent within 0·01 Å) which agree quite well with the experimental ones [2], cf. table 3. In contrast to the hydrocarbons studied in [13] the calculated bond lengths of kekulene in the lowest triplet state are not significantly different from those in the ground state. Using the experimental bond lengths we obtain $D = 0·101$ cm^{-1} in fair agreement with experiment.

We would expect $D \approx 0·045$ cm^{-1} for a linear polyacene with about the same number of carbon atoms as kekulene and a polynomial, which was obtained by a least squares fit to all D values in [13], yields $D \approx 0·07$ cm^{-1} for kekulene. The increase to 0·089 cm^{-1} within the approximation of fixed bond lengths has two reasons : (i) Kekulene is a highly symmetrical molecule which leads generally to a higher D-value [13]. (ii) The bond lengths in the ground and triplet states (cf. table 2) are compatible with the sextet notation in figure 1, i.e. we have both six equivalent sextets and quasi localized double bonds (in Clar's notion [16]) similar to phenanthrene. The contributions to $|D|$ of the two sextets and the quasi localized double bond in phenanthrene are 0·0599 and 0·0414 cm^{-1}, respectively. These values are similar to the corresponding contributions of the sextets and quasi localized double bonds in kekulene, 0·0580 and 0·0302 cm^{-1}, respectively. Thus these highly localized double bonds, which are described by molecular orbitals being singly occupied in the leading configuration of the triplet wavefunction, make up already 39 per cent of the total $|D|$ value of phenanthrene and 30 per cent of kekulene. The use of the actual bond lengths increases all bond contributions to $|D|$; the effect being somewhat more pronounced for the sextets than for the quasi localized double bonds.

The calculated mean separation of the two unpaired electrons in the lowest triplet state of kekulene and phenanthrene are very similar, i.e. 2·62 and 2·56 Å, respectively. This corresponds to the close agreement of the D-values although there is no general simple relationship between both quantities [13].

Comparison of the phosphorescence emissions in figures 5 (*a*) and 5 (*b*) shows that, after irradiation for some hours with U.V.-light, a number of additional phosphorescence peaks appear, some of which were also observed in untempered samples. These additional phosphorescence peaks are due to additional kekulene sites which are probably created by a reorientation after excitation and deactivation of kekulene molecules in the polycrystalline matrix. Such a reorientation seems quite possible because the large kekulene molecules are enclosed in cavities of different sizes, replacing several tetrachlorobenzene molecules. By plotting the zero-field splitting parameters, D and E, of the different sites as a function of their $S_0 - T_1$ energy differences (figure 6), a few interesting points can be noticed. The zero-field splitting parameters are, in first order, linearly proportional to the $S_0 - T_1$ energies. The weak emission peak at 17 117·4 cm^{-1} (w in figure 6) appears with higher sensitivity already in the fresh sample spectrum (figure 5 (*a*)). The position of this peak (w) on the straight line in figure 6 seems to indicate that this is not the site where kekulene molecules possess a sixfold symmetry (ODMR experiments on this peak were not possible because of the weakness of the emission). The position for such a site would be around 17 160 cm^{-1}.

The variation of the energy of the 0–0 bands of the phosphorescences of the different sites are about 250 cm^{-1} at the maximum. It seems that the stronger

the deviations from sixfold symmetry of kekulene in a given site, the lower is the energy of the corresponding triplet state. This behaviour might be discussed in terms of a recently suggested model, in which the optical energy distribution and the ODMR microwave transition frequencies are related by spin-orbit interaction. This model [17], used for explaining the broadening of optical and ODMR transitions of guest molecules in host lattices by random spin-orbit interactions caused by electronic energy fluctuations in the singlet and triplet states, seems to be related to our problem, although the sublevels of the lowest triplet state of kekulene are more strongly coupled to the singlet states by spin-orbit interaction, due to a strong heavy atom effect of the chlorine atoms of the tetrachlorobenzene host matrix than in usual Shpol'skii-matrices.

Using the nomenclature of Lemaistre and Zewail [17], we describe the electronic energies of the first excited singlet and triplet states of the different sites (i) by

$$E_i^{(r)} = E_0^{(r)} + \Delta_i^{(r)} \quad (i = 1, 2, 3 \ldots),$$ (1)

where r denotes the singlet (S) or the triplet (T) state of the different sites (i) and $E_0^{(r)}$ is the energy of one selected special site (for example, the site with the highest energy).

$\Delta_i^{(r)}$ corresponds to the energy difference between the considered sites (0) and (i). The distribution E_i^S may or may not be correlated with the distribution of E_i^T.

We assume that each molecule has only one magnetic sublevel σ_x (in our case the top level) of its triplet state actively coupled through spin orbit coupling (SOC) to a singlet state. This assumption is in any case justified for those sites in which only one of the triplet sublevels radiates [10]. Accordingly, using perturbation theory we obtain, following Lemaistre and Zewail [17], for the uncorrelated case for the ODMR transition frequency between the spin orbitally active magnetic sublevel (σ_x) and the inactive sublevel σ_j ($j = y, z$)

$$\hbar \omega_{xj}{}^i = \hbar \omega_{xj}{}^0 + |b_0|^2 \cdot (\Delta_i^{(S)} - \Delta_i^{(T)})$$ (2)

with $\omega_{xj}{}^0$ being the ODMR transition of the specially selected site (0) with energies $E_0^{(r)}$ and b_0 the SOC mixing coefficient for this site.

If the distribution E_i^S is correlated with the distribution E_i^T by

$$\Delta_i^{(T)} = \alpha \Delta_i^{(S)}$$ (3)

we obtain

$$\hbar \omega_{xj}{}^i = \hbar \omega_{xj}{}^0 + |b_0|^2 \cdot \left(\frac{1 - \alpha}{\alpha}\right) \Delta_i^{(T)}.$$ (4)

The inhomogeneous linewidth $\Lambda_{xj}{}^{(i)}$ of the ODMR transition in this case is given by [17].

$$\Lambda_{xj}{}^{(i)} = |b_0|^2 \cdot \left(\frac{1 - \alpha}{\alpha}\right) \cdot \Lambda_T{}^{(i)},$$ (5)

where $\Lambda_T{}^{(i)}$ is the optical triplet linewidth of site (i) which may be inhomogeneously broadened and hence has a gaussian distribution.

Von Borczyskowski *et al.* [18] have discussed the influence of a vibronic coupling with energetically close $n\pi^*$ triplet states on the zero field splitting of the lowest triplet state. Since the ZFS is very little affected by coupling with

$\pi\pi^*$ states and since in the kekulene molecule $n\pi^*$ triplet states do not exist, the contributions of these interactions should be rather small, if any.

Using site I as the special selected site with the triplet energy $E_0{}^T = 17\,073 \cdot 3$ cm^{-1} and as site (i) the one with $E_1{}^T = 17\,093 \cdot 3$ cm^{-1} (see table 1), both of which have only one radiative triplet sublevel in the 0–0 band, and taking $\alpha = 0 \cdot 78$ in equation (3), we get, from the $2E$ transitions, a SOC mixing coefficient $b_0 = 1 \times 10^{-2}$ and from the $D + E$ transitions $b_0 = 1 \cdot 2 \times 10^{-2}$. On the other hand, using the optical linewidth of $2 \cdot 3$ cm^{-1} for the 0–0 band of site I and the ODMR linewidth of $2 \cdot 1$ MHz (see figure 4), we obtain independently from equation (5) $b_0 = 1 \cdot 04 \times 10^{-2}$ which is in good agreement with the above values.

Taking the values for site I and site II (table 1), the two calculated SOC mixing coefficients are $b_0 = 8 \cdot 3 \times 10^{-3}$ from the $2E$ transitions and $b_0 = 5 \cdot 7 \times 10^{-3}$ from the $D + E$ transitions. These values do not agree as well as in the first case, which might be due to the fact that all sites with triplet energies lower than site I have at least two strongly radiative triplet sublevels. Therefore, the assumption that only one magnetic triplet sublevel is actively coupled to the singlet state through SOC is not fulfilled and hence the case of two channel SOC [17] should be considered.

Nevertheless, a SOC mixing coefficient b_0 of the order of 10^{-2} seems to be not unlikely because of the strong intermolecular heavy atom effect of the chlorine atoms of the host matrix on the kekulene molecules.

Kekulene in tetrabromobenzene cannot be analysed in such a simple way because no fluorescence could be observed. This fact shows that the intermolecular heavy atom effect is much stronger in this matrix and therefore the SOC mixing coefficient b_0 is probably still larger than 10^{-2}. It is perhaps worth noticing that the E-value of $0 \cdot 00074$ cm^{-1} corresponding to a frequency of $22 \cdot 07$ MHz (see figure 4 (b)) for the site at $16\,886 \cdot 1$ cm^{-1} is one of the smallest observed so far in triplet states of planar aromatic molecules.

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