lar structure of kekulene by X-ray analysis was of special interest.

(1) crystallized from pyrene (purified by zone-melting) in a tube sealed under high-vacuum on slow cooling from 450 to 350 °C. Removal of pyrene by high-vacuum sublimation and washing the crystals with chloroform yielded yellow monoclinic needles suitable for a structure analysis [crystal size $0.05 \times 0.08 \times 0.4$ mm; space group C2/c; $a = 2799(3)$, $b = 458.7(5)$, $c = 2271(2)$ pm, $\beta = 109.6(1)°$, $Z = 4$, $\rho_{calc.} = 1.45$ g·cm^{-3}; Mo$_{K\alpha}$ radiation, 1596 observed reflections, $R = 0.056$].
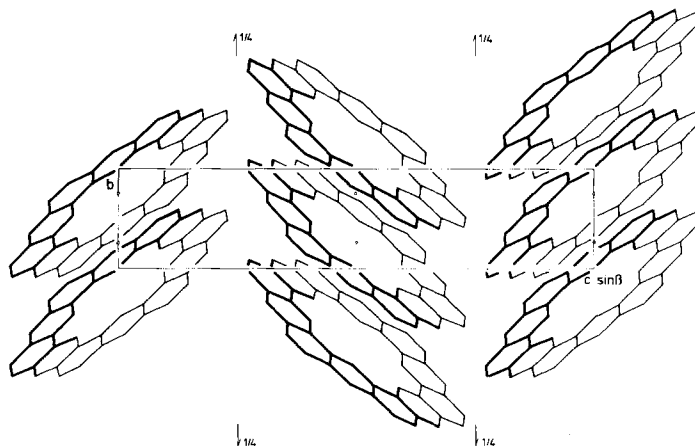

Fig. 1. Lattice structure of *(1)* as projected along the a axis (the rear half of the unit cell is not drawn).

Molecular Structure and Spectroscopic Properties of Kekulene[1]

By *Claus Krieger, Francois Diederich, Dieter Schweitzer,* and *Heinz A. Staab*[*]

Kekulene *(1)*, the synthesis of which was recently reported[2], is the first example of a new class of aromatic compounds in which the annellation of six-membered rings leads to a cyclic system enclosing a cavity lined with hydrogen atoms. Compound *(1)*, for which 200 Kekulé structures with different arrangements of double and single bonds can be formulated[3], was of interest with regard to π-electron delocalization and the related problem of the diatropicity in the macrocyclic system for which, as long ago as 1951, different theoretical approaches were shown to lead to contradictory predictions in the specific case of *(1)*[4]. Experimentally, the ^{1}H-NMR absorption of the internal hydrogens did not show any evidence for a diatropicity in the macrocyclic system[2], in qualitative agreement with MO calculations of chemical shifts[4, 5]. In this context, and in connection with some spectroscopic properties of *(1)*, the determination of the molecu-
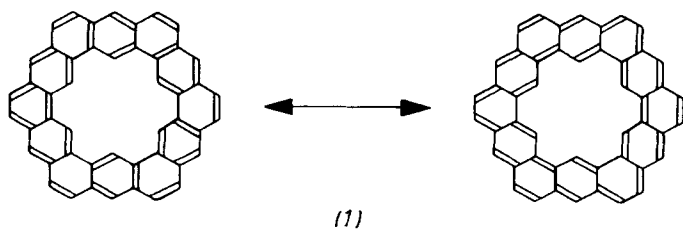
In the crystal lattice of *(1)* the molecules are stacked along the b axis with the stacking axis forming an angle of 42.9° with the molecular planes. Neighboring molecules in such a stack have an interplanar distance of 336 pm and are parallel-shifted by 312 pm. The molecular planes of adjacent stacks are inclined by 86° to each other, resulting in the "herringbone pattern" shown in Figure 1 as a side view along the a axis.

With a mean deviation of carbon atoms from the mean plane through the 48 carbon atoms of only 3 pm and a maximum deviation of 7 pm, *(1)* has an almost perfectly planar structure. This includes, with deviations of 5 and 10 pm, respectively, even the six internal hydrogens, although the non-bonding distances of 196(2) pm between adjacent hydrogen atoms are unusually short.
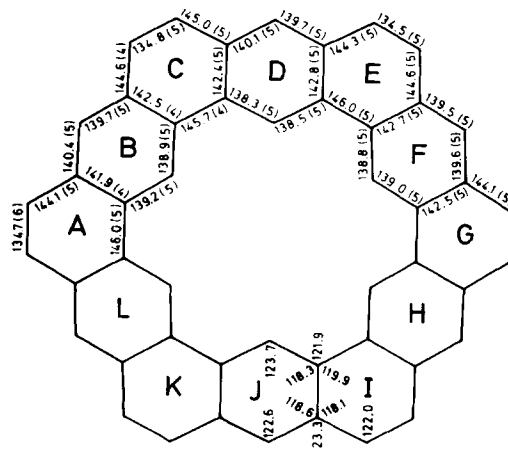

(1)

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Fig. 2. Bond lengths of *(1)* in pm (standard deviations in units of the last figure given in brackets) and valence angles (as mean values of equivalent angles).

Figure 2 shows clearly that there is a remarkable difference between the bond lengths in the two groups of six-membered rings A, C, E, G, I, K and B, D, F, H, J, L. Only in the last-mentioned group, with mean values of 138.8 pm for the bonds of the internal (1)-perimeter and of 139.8 pm for the bonds of the external perimeter, are "normal" arene bond lengths observed; even here, all six radial bonds, having a mean value of 142.3 pm, are significantly stretched. Drastic deviations from the bond lengths of these "aromatic rings" (B, D,...), however, are found for the second group of six equivalent six-membered rings (A, C,...): The six peripheral CH—CH bonds of these rings have a mean value of 134.6 pm, i.e. almost the length of a normal C=C double bond; correspondingly, a mean length of 144.5 pm for the bonds between these "double bonds" and the "aromatic rings" (B, D,...) indicates a relatively high single bond character. An even stronger extension is found for the bonds (about 146 pm) which link the "aromatic rings" in the inner perimeter; they accordingly approach single bonds of the type found in polyphenyl systems.

Considering the number of 200 possible Kekulé structures of (1), the considerable bond localization evident from the bond lengths might seem surprising. The observed variation in bond lengths was, however, predicted in its qualitative trend—though not in the extent actually found—by MO-SCF calculations[6]. Excellent agreement with the experimental bond lengths was found on evaluation of the Kekulé structures with regard to Pauling bond orders of the individual bonds in (1)[7]. On the basis of the structure analysis, a formulation employing Clar's sextet notation (1a) is undoubtedly the best representation of the actual bonding situation in kekulene.

(1a)
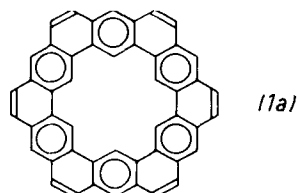
Some spectroscopic properties of kekulene also agree well with the sextet formulation (1a): The electronic spectrum of (1) shows an absorption at remarkably short wavelength as is generally observed, according to Clar[8], for arenes of the "condensed polyaryl type", such as hexabenzocoronene (Fig.
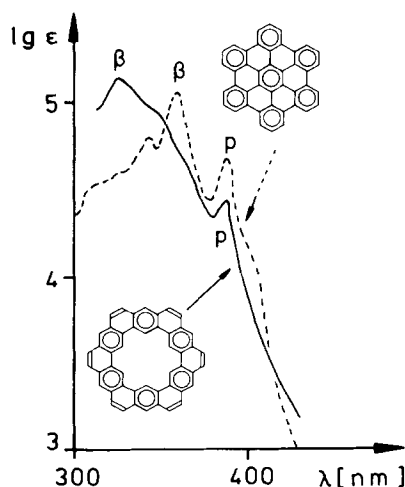
3). The symmetry-forbidden α-band of (1) is obviously hidden under the long-wavelength part of the p-band; however, the strongly vibrationally structured fluorescence band at 453 nm evidently has to be assigned to this α-transition (Fig. 4a).

Just as hexabenzocoronene shows a strong phosphorescence at 575 nm (in 1,2,4-trichlorobenzene) at low temperatures[8], compound (1) in a [D$_2$]-1,2,4,5-tetrachlorobenzene matrix at 1.3 K exhibits a strong phosphorescence emission in the range 585—595 nm with several narrowly spaced "site"-dependent maxima and a vibrational structure resulting from combination with molecular vibrations in the range 1280—1630 cm^{-1} (Fig. 4b).
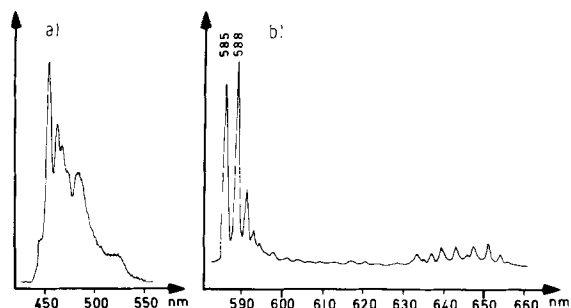

Fig. 4. a) Fluorescence spectrum of (1) (in 1,2,4-trichlorobenzene, 298 K, excitation 326 nm); b) phosphorescence spectrum of (1) (in [D$_2$]-1,2,4,5-tetrachlorobenzene, 1.3 K, excitation 365 nm); intensities in arbitrary units.

The strong phosphorescence of (1) permits application of the ODMR method for the determination of zero field splitting parameters |E| and |D| of the excited triplet state[9]. For (1) in a [D$_2$]-1,2,4,5-tetrachlorobenzene matrix, an |E| value of 0.001935 cm^{-1} was obtained which, as expected from the D$_{6h}$ symmetry of (1), is very low (benzene: |E| = 0.0064 cm^{-1}). However, the |D| value—which measures the dipolar coupling of the triplet electrons and, therefore, is inversely proportional to the third power of the average distance between these electrons—found for kekulene [|D| = 0.10622 cm^{-1}] is only slightly lower than for benzene and even greater than |D| for naphthalene and anthracene (cf. benzene 0.1581, naphthalene 0.0994, anthracene 0.0694 cm^{-1}). This unexpectedly small reduction of |D| in (1)[10] is very striking at first sight, considering the wide spatial extension of the π-electron system in kekulene. We seek to explain this result qualitatively as an effect of the partial compartmentization of the π-electron system in (1) as suggested by the X-ray structure analysis[11].

[1] Conjugation in Macrocyclic Systems, Part 30.—Part 29: H. A. Staab, U. E. Meissner, A. Gensler, Chem. Ber., in press.
[2] F. Diederich, H. A. Staab, Angew. Chem. 90, 383 (1978); Angew. Chem. Int. Ed. Engl. 17, 372 (1978).—W. Jenny, P. Baumgartner, R. Paoni (ISNA-Proc., Sendai/Japan, August 1970) claimed, without giving any details, to have prepared kekulene (1)—which they named "[12]coronaphene"—as long ago as 1970. Since other authors (cf., for example, [3]) refer to this claim we are compelled to make the following statement: The authors named have until now published neither a synthesis of (1) nor any account of its properties in the chemical literature. Although they have not repeated their claim to the synthesis of (1) in later topically related publications, they have failed so far to withdraw this claim.
[3] J. Aihara, Bull. Chem. Soc. Jpn. 49, 1429 (1976).
[4] R. McWeeny, Proc. Phys. Soc. London A 64, 261, 921 (1951), and references given therein.
[5] G. Ege, H. Vogler, Theor. Chim. Acta 26, 55 (1972); H. Vogler, Tetrahedron Lett. 1979, 229; C. Wilcox, personal communication.
[6] G. Ege, H. Fischer, Tetrahedron 23, 149 (1967).
[7] We thank Prof. W. C. Herndon, University of Texas at El Paso, for stimulating discussions.

Fig. 3. Absorption spectra of (1) and hexabenzocoronene (in 1,2,4-trichlorobenzene).

[8] *E. Clar:* Polycyclic Hydrocarbons, Vol. 2. Academic Press, New York/ Springer-Verlag, Berlin 1964, p. 97.

[9] Concerning the ODMR method, see references in *D. Schweitzer, K. H. Hausser, V. Taglieber, H. A. Staab,* Chem. Phys. *14,* 183 (1976).

[10] Regarding these results with *(1)* it is interesting that similar ODMR results have been obtained recently with hexabenzocoronene and related aromatic hydrocarbons of the "polyaryl type" with high molecular symmetry: *J. Voitländer,* personal communication.

[11] Attempted theoretical treatment of this hypothesis: *H. Vogler,* Symposium on Aromaticity, Dubrovnik, September 1979.