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Cycloarenes, a New Class of Aromatic Compounds, II[1]

Molecular Structure and Spectroscopic Properties of Kekulene

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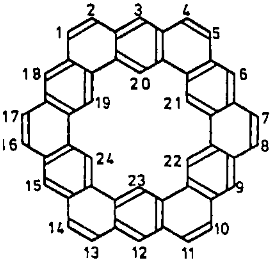
The molecular structure of kekulene (**1**) was determined by X-ray structure analysis. From the bond lengths of **1** a remarkable localisation of aromatic sextets and double bonds is concluded (cf. formula **1b**). – The problem of annulenoid versus benzenoid diatropicity in **1** is discussed on the basis of ^{1}H NMR absorptions. These data, in agreement with recent theoretical calculations, support a predominant ring-current induction in the benzenoid subunits of **1** and rule out a significant contribution of annulenoid structures like **1a**. – Absorption and emission spectra of **1** are discussed as are the zero-field splitting parameters of the excited triplet state of **1**.

Cycloarene, eine neue Klasse aromatischer Verbindungen, II[1]

Molekülstruktur und spektroskopische Eigenschaften von Kekulen

Die Molekülstruktur von Kekulen (**1**) wurde durch Röntgen-Strukturanalyse bestimmt. Aus den Bindungslängen von **1** wird auf eine bemerkenswerte Lokalisation von aromatischen Sextetts und Doppelbindungen im Sinne der Formulierung **1b** geschlossen. – Das Problem der annulenoiden oder benzoiden Diatropie von **1** wird an Hand der ^{1}H-NMR-Spektren diskutiert. Die experimentellen Ergebnisse stützen in Übereinstimmung mit neueren theoretischen Berechnungen die Annahme einer vorherrschenden Ringstrom-Induktion in den benzoiden Untereinheiten von **1** und schließen einen wesentlichen Beitrag annulenoider Strukturen wie **1a** aus. – Absorptions- und Emissionsspektren von **1** sowie Nullfeld-Aufspaltungsparameter des angeregten Triplettzustands von **1** werden diskutiert.

In the preceding paper[1] we described the synthesis of kekulene (**1**) which is the first example of "cycloarenes". This new class of aromatic compounds is defined as comprising aromatic systems in which the circular annellation of arene units results in a



1

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macrocyclic structure enclosing a cavity surrounded by carbon-hydrogen bonds. According to the nomenclature we suggested for cycloarenes[1] the systematic name of **1** is "cyclo[*d.e.d.e.d.e.d.e.d.e.d.e*]dodecakisbenzene".

In this paper we report on the molecular structure of **1** as derived from X-ray structure analysis and discuss ^{1}H NMR spectra and other spectroscopic data which are relevant to the electronic structure of **1**.

Molecular and Crystal Structure of 1[2]

Crystal Preparation and X-Ray Structure Analysis: Due to the extremely low solubility of **1** in all solvents it was extraordinarily difficult to obtain single crystals of **1** suitable for an X-ray analysis. Eventually **1**-crystals were grown from pyrene by slow cooling from 450 to 350°C and preparing the crystals as described in detail in the Experimental Part. **1** forms monoclinic needles with the following cell parameters: a = 2795.1 (4), b = 457.9 (1), c = 2268.0 (2) pm, β = 109.64 (1); space group $C2/c$; Z = 4; D_x = 1.46 gcm^{-3}. Intensity data were collected using graphite-monochromated Mo-K_α radiation (Enraf-Nonius CAD 4). Up to $\sin \Theta/\lambda$ = 6.98 nm^{-1} 3803 symmetry-independent reflections were measured out of which 1560 reflections with $I \geqslant 1.92\sigma(I)$ were graded as observed.

Table 1. Atomic Coordinates and Thermal Parameters (in pm^2) for Carbon Atoms and for Hydrogen Atoms of **1** (in Brackets Standard Deviations in Units of the Last Quoted Digit)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
C(1)	0.17207(7)	1.0897(5)	0.27390(8)	438(7)	C(13)	0.18988(7)	-0.4944(5)	0.63015(8)	364(6)
C(2)	0.12601(7)	0.9874(5)	0.27051(8)	422(7)	C(14)	0.23430(7)	-0.5920(5)	0.67536(8)	404(7)
C(3)	0.11987(6)	0.7740(5)	0.31410(8)	356(7)	C(15)	0.28224(6)	-0.4911(5)	0.67861(8)	357(7)
C(4)	0.07298(7)	0.6605(5)	0.31217(8)	394(7)	C(16)	0.21391(6)	0.7853(5)	0.36621(7)	332(6)
C(5)	0.06793(6)	0.4529(5)	0.35486(8)	363(7)	C(17)	0.16411(6)	0.6740(5)	0.36212(7)	315(6)
C(6)	0.01930(7)	0.3308(5)	0.35304(8)	453(7)	C(18)	0.15855(6)	0.4680(5)	0.40406(8)	352(7)
C(7)	0.01570(6)	0.1407(5)	0.39552(9)	449(7)	C(19)	0.11232(6)	0.3523(5)	0.40228(8)	326(6)
C(8)	0.05953(6)	0.0314(5)	0.44481(8)	365(7)	C(20)	0.10788(6)	0.1367(5)	0.44716(8)	328(6)
C(9)	0.05637(7)	-0.1726(5)	0.48900(8)	411(7)	C(21)	0.15044(6)	0.0287(5)	0.49298(8)	355(7)
C(10)	0.09979(6)	-0.2765(5)	0.53532(8)	365(6)	C(22)	0.14836(6)	-0.1763(5)	0.53720(8)	318(6)
C(11)	0.09739(7)	-0.4850(5)	0.58167(8)	433(7)	C(23)	0.19369(6)	-0.2899(5)	0.58519(8)	332(6)
C(12)	0.13933(7)	-0.5874(5)	0.62609(8)	441(7)	C(24)	0.24161(6)	-0.1934(5)	0.58821(8)	378(7)

Atom	x	y	z	Uiso.	Atom	x	y	z	Uiso.
H(1)	0.1751(5)	1.240(4)	0.2429(6)	689(70)	H(11)	0.0630(5)	-0.552(4)	0.5882(6)	476(60)
H(2)	0.0949(5)	1.059(4)	0.2378(6)	430(50)	H(12)	0.1383(5)	-0.726(4)	0.6592(6)	670(60)
H(4)	0.0422(4)	0.738(3)	0.2803(6)	322(50)	H(14)	0.2310(5)	-0.738(4)	0.7067(6)	463(60)
H(6)	-0.0123(5)	0.411(4)	0.3203(6)	626(60)	H(18)	0.1889(4)	0.397(3)	0.4371(5)	284(40)
H(7)	-0.0179(5)	0.070(4)	0.3943(6)	523(60)	H(21)	0.1852(5)	0.094(3)	0.4939(5)	309(50)
H(9)	0.0215(5)	-0.249(4)	0.4875(6)	610(60)	H(24)	0.2449(5)	-0.050(4)	0.5565(6)	339(50)

A solution of the structure was not possible by using direct methods. From a Patterson synthesis, however, the position of the molecular planes in the elementary cell and an interplanar distance of the **1**-molecules of approximately 340 pm were derived. The model based on the molecular C_i symmetry of **1** then was improved by slightly turning the rigid molecule around the central symmetry axis (normal to the molecular plane). Full-matrix least-squares refinement of the atomic coordinates using anisotropic thermal parameters for the carbon atoms and isotropic thermal parameters for the hydrogen atoms led to a convergence at $R = 0.052$. Atomic coordinates and thermal parameters for the carbon and hydrogen atoms of **1** are listed in Table 1 (for the numbering of atoms see Figure 3)[3].

Crystal Lattice of **1**: In the **1**-crystals the molecules are stacked along the *b*-axis with the stacking axis forming an angle of 42.9° with the molecular planes. Within such a stack of equidistant molecules the interplanar distance is 335 pm; neighbouring molecules are parallel-shifted by 312 pm resulting in an overlap as shown in Figure 1. The molecular planes in adjacent stacks are inclined to each other by 86°. Thus, a typical "herringbone pattern" results which is shown in Figure 2 in a view along the *a*-axis.

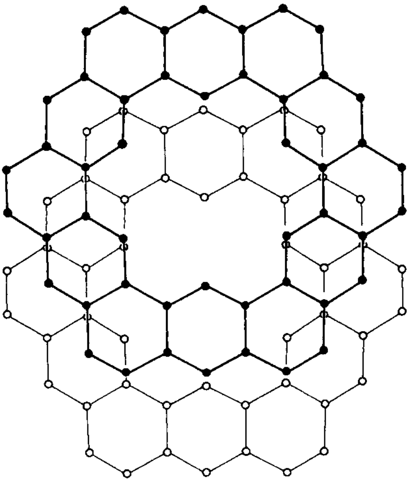


Figure 1. Overlap Diagram of Two Neighbouring **1**-Molecules

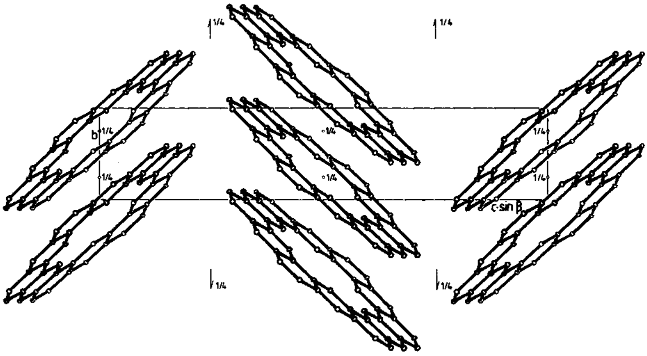


Figure 2. Crystal Packing of **1** as Shown in the Projection along *a* (for the Sake of Clearness Only Stacks Centered at 1/4 *a* are Drawn; Corresponding Stacks at 3/4 *a* which Result from C-Centration are Omitted)

Molecular Structure of **1**: The kekulene molecule has an almost perfectly planar structure. The mean deviation of the carbon atoms from the least-squares plane through all 48 carbon atoms amounts to only 3 pm; the maximum deviation from this plane is 7 pm. The close approach to planarity includes even the six internal hydrogens

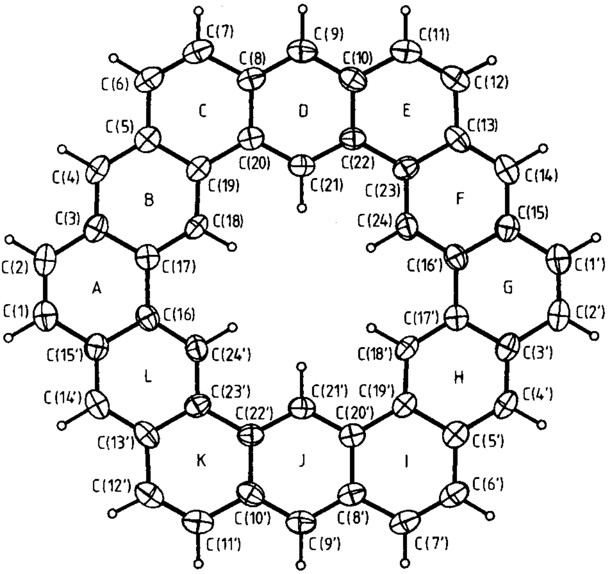


Figure 3. ORTEP Plot of **1**

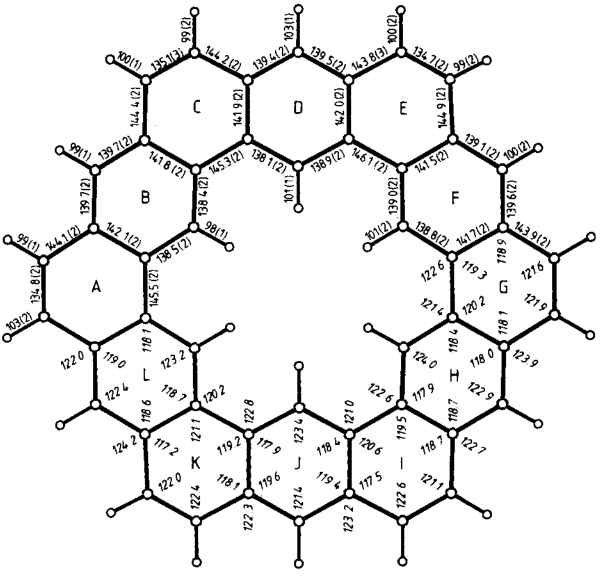


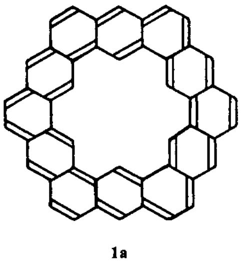
Figure 4. Bond Lengths (in pm) and Bond Angles (in °) of **1**

(maximum deviation 9 pm) although the non-bonding distances between adjacent hydrogens in the central cavity of **1** with 192 (2) pm are unusually small.

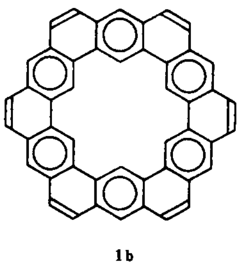
With regard to the electronic structure of **1** the carbon-carbon bond lengths in **1** were of special interest. From the data given in Figure 4 it is seen that there is a remarkable difference in bond lengths between the two groups of benzene units A,C,E,G,I,K and B,D,F,H,J,L, respectively. Only for the last mentioned group "normal" arene bond lengths are oberved; for these rings the mean value for carbon-carbon bonds in the outer perimeter amounts to 139.5 (2) pm, that of the bonds in the inner perimeter to 138.6 (3) pm whereas the radial bonds are slightly stretched to a mean value of 141.8 (2) pm. Drastic differences to the bond lengths of these "aromatic" rings, however, are found for the second group of six-membered rings in **1** (A,C, ...). The six peripheral carbon-carbon bonds of these rings [C(1)···C(2), C(6)···C(7) etc.], with a mean bond length of 134.9 (2) pm, have almost the length of normal carbon-carbon double bonds. For the bonds [C(2)···C(3), C(5)···C(6) etc.] linking these "double bonds" to the "aromatic" rings (B,D, ...) a mean length of 144.2 (4) pm is found indicating a relatively high single bond character. An even stronger extension to a mean bond length of 145.6 (4) pm is observed for the bonds which connect the "aromatic" rings in the inner perimeter [C(16)···C(17), C(19)···C(20) etc.]; these bonds approach the type of single bonds found in polyphenyl systems.

In view of the fact that for **1** 200 Kekulé structures with different arrangements of single and double bonds can be formulated4) the considerable bond localisation as shown by the experimental bond lengths might seem surprising at first sight. The observed variation of bond lengths was, however, predicted by MO-SCF calculations5) in its qualitative trend though not to the extent actually found. Very good agreement with the experimental bond lengths results from an evaluation of Kekulé structures with regard to Pauling bond orders derived for the individual bonds in **1**6).

On the basis of the X-ray analysis there is no indication to any significant contribution of structures in which two [4n + 2]annulene perimeters are linked by radial single bonds (**1a**). Instead, a formulation using *Clar*'s sextet notation7) (**1b**) is undoubtedly the best representation of the actual bonding state of kekulene.



1a



1b

^{1}H NMR Results Concerning the Diatropicity of 1

As pointed out in the preceding paper1) our interest in cycloarenes was aroused by the problem of annulenoid versus benzenoid aromaticity and by the fact that there existed divergent predictions with regard to the diatropicity of **1**8). Using the protons in the inner cavity as a probe it should be possible to decide experimentally whether an annulenoid diatropicity in the macrocyclic system might prevail over the ring-current induction within the benzenoid subunits in **1**.

^{1}H NMR spectra, recorded under extraordinary conditions due to the extreme insolubility of **1**[1], showed three signals in the intensity ratio 2:1:1 at δ = 7.95, 8.37, and 10.45 in [D_3]-1,3,5-trichlorobenzene at about 200°C, and at δ = 8.01, 8.45, and 10.47 in [D_2]-1,2,4,5-tetrachlorobenzene at 155°C, respectively. Accordingly, there is no signal shifted strongly upfield as would be expected for the internal protons in case of a strong diatropicity of the macrocyclic system. On the contrary, on the basis of the intensity ratio and a comparison with macrocyclic precursor molecules of **1**[1] the signal at lowest field (δ = 10.47, in [D_2]-1,2,4,5-tetrachlorobenzene) is assigned to the six internal protons 19,20,21,22,23,24-H; on the same basis the signal at δ = 8.45 was attributed to the six protons 3,6,9,12,15,18-H, and the signal at δ = 8.01 to the remaining 12 equivalent external protons 1,2,4,5,7,8,...-H (for the numbering of atoms see formula **1**). The peculiar downfield shift just of the inner protons is taken as a strong experimental argument against a predominant ring-current induction in the macrocyclic system. It is, however, in accordance with these protons being positioned in the deshielding region of quasi-localized benzenoid subunits as revealed by the structure analysis (cf. formula **1b**).

Table 2 shows a quantitative comparison of experimental ^{1}H-chemical shifts with recently calculated δ-values. Column I applies to calculations with a modified Hückel MO theory[9]; the data given under II take into account an additional van der Waals deshielding[10] for the sterically overcrowded inner hydrogens. Columns III and IV, respectively, list chemical shifts calculated by *Wilcox*[11] on the basis of the McWeeny ring-current analysis and by *Vogler*[12] within the coupled Hartree-Fock perturbation theory, both considering van der Waals corrections for the internal hydrogens. The latter approach leads to a rather satisfying agreement between experiment and theory for the outer as well as the inner protons in **1**. These results confirm that resonance structures like the double annulene structure **1a** do not contribute significantly in **1**.

Table 2. Experimental and Calculated ^{1}H-Chemical Shifts
[a) in [D_2]-1,2,4,5-Tetrachlorobenzene, 155°C; b) See Text for Explanation]

		$\delta^{b)}_{Calc.}$			
	$\delta^{a)}_{Exp.}$	I	II	III	IV
1,2...-H	8.01	8.01	8.01	7.70	8.22
3,6...-H	8.45	8.78	8.78	8.25	8.71
19,20...-H	10.47	8.67	9.87	10.26	10.42

Absorption and Emission Spectra; Zero Field Splitting Parameters of 1[13]

The absorption spectrum of **1** ($4 \cdot 10^{-7}$ M solution in 1,2,4-trichlorobenzene, 10 cm cell) is shown in Figure 5. With its remarkably short wavelength the absorption corresponds to the spectra of condensed polycyclic aromatic hydrocarbons of the "polyaryl type" like hexabenzocoronene[14]. The α-band of **1**, symmetry-forbidden due to the D_{6h}

symmetry, is not observed under the experimental conditions applied. The α-transition is, however, observed in fluorescence as a strongly vibrationally structured band with λ_{max} = 453 nm (excitation 326 nm). Fluorescence as well as phosphorescence emissions of **1** in 1,2,4,5-tetrachlorobenzene at 1.3 K are shown in Figure 6[2,13]. The relatively strong emission from T_1 in the range of 585 – 595 nm is also visible as an orange phosphorescence at room temperature in solid solutions of **1** (≈ 10^{-6} M) in 1,3,5-trichlorobenzene and other chlorinated benzenes.

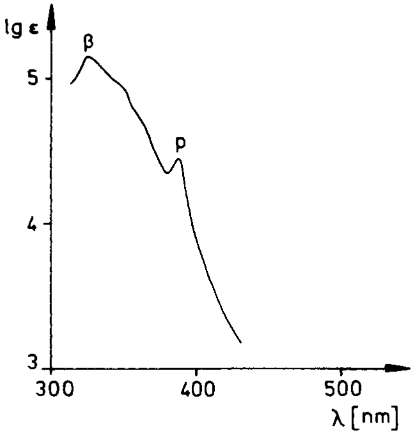


Figure 5. Absorption Spectrum of **1** in 1,2,4-Trichlorobenzene ($4 \cdot 10^{-7}$ M, 10 cm cell)

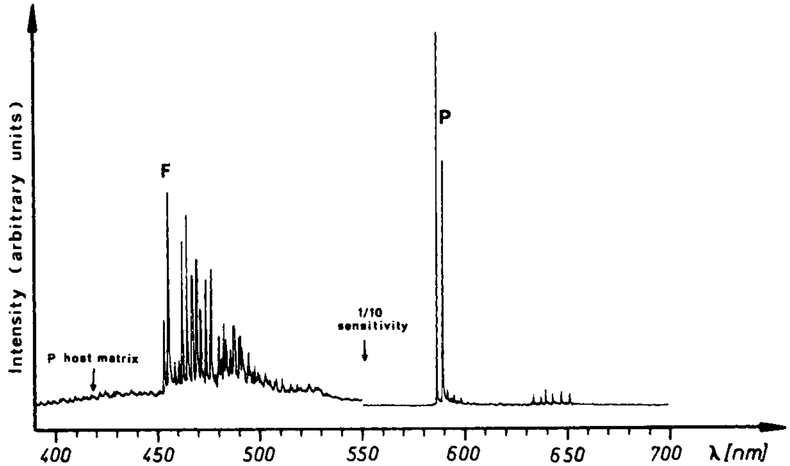


Figure 6. Fluorescence (F) and Phosphorescence (P) of **1** in 1,2,4,5-Tetrachlorobenzene (1.3 K)[13]

The strong phosphorescence of **1** permitted the application of the ODMR method for the determination of zero field splitting parameters $|D|$ and $|E|$ of the excited triplet state[13]. The $|D|$ value measures the dipolar coupling of the triplet electrons and, therefore, is a function of the inverse average distance between these electrons. Accordingly, the $|D|$ values decrease with increasing extension of π-electron systems (e.g., benzene: 0.1581 cm^{-1}; naphthalene: 0.0994 cm^{-1}; anthracene: 0.0694 cm^{-1}). Considering the wide spatial extension of the π-electron system in **1** the $|D|$ parameter for **1** was found to be surprisingly high (0.1039 cm^{-1}; in 1,2,4,5-tetrabromobenzene, 1.3 K). As has been substantiated theoretically[13,15], this result was interpreted in terms of the partial compartmentalization of the π-electron system of **1** into quasi-localized aromatic sextets and double bonds. Thus, these data, too, are in accordance with the molecular structure of **1** as derived from X-ray structure analysis.

The support of this project by *Stiftung Volkswagenwerk,* Hannover, and *Fonds der Chemischen Industrie,* Frankfurt am Main, is gratefully acknowledged. We thank *H. Zimmermann* of our Institute for supplying the zone-refined solvents used in this investigation and for his help in the preparation of single crystals of **1**.

Experimental Part

Growing of **1**-*crystals:* 7 mg of **1** and 2 g of zone-refined pyrene were placed in a glass-tube and degassed by four freeze-pump-melt cycles at 10^{-5} torr. After sealing off under high-vacuum the glass-tube was heated to 450°C. Slowly cooling down within 24 h from 450 to 150°C (inside of a heating spiral) led between 400 and 350°C to the formation of needles of **1**. After cooling the tube was opened and placed into a sublimation apparatus to remove the pyrene by sublimation at 120°C/10^{-3} torr. To the residue chloroform was added, and the crystals of **1** were isolated by filtration, washed several times with chloroform and dried at 50°C/10^{-3} torr: 6.9 mg of **1** as golden-yellow needles (length up to 3 mm). For the X-ray structure analysis a single crystal of the size 0.05 × 0.08 × 0.4 mm was used.

Alternatively, by applying the same procedure, crystals of **1** could also be obtained from a solution in triphenylene (purified twice by sublimation).

1-*Solution for Absorption and Emission Spectra:* To obtain a $4 \cdot 10^{-7}$ M solution 0.012 mg of **1** was heated under nitrogen for 3 h to 200°C in 50 ml of 1,2,4-trichlorobenzene (purified twice by distillation).

1-*Solution in 1,2,4,5-Tetrachlorobenzene Matrix:* 0.02 mg of **1** and 2 g of zone-refined 1,2,4,5-tetrachlorobenzene were heated under nitrogen 3 d to 180°C. After filtering off undissolved **1** the sample for recording the emission spectra at 1.3 K was obtained by rapidly cooling the solution.

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1) Part I: *H. A. Staab* and *F. Diederich,* Chem. Ber. **116,** 3487 (1983), preceding.

2) For preliminary results cf. *C. Krieger, F. Diederich, D. Schweitzer,* and *H. A. Staab,* Angew. Chem. **91,** 733 (1979); Angew. Chem., Int. Ed. Engl. **18,** 699 (1979).

3) Further information concerning the X-ray structure analysis of **1** may be requested from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, with indication of the registry number CSD 50453, the authors' names and the journal citation.

4) See *J. Aihara,* Bull. Chem. Soc. Jpn. **49,** 1429 (1976).

5) *G. Ege* and *H. Fischer,* Tetrahedron **23,** 149 (1967).

6) *W. C. Herndon,* personal communication; see also lit.4).

7) Cf. *E. Clar,* Polycyclic Hydrocarbons, Vols. 1 and 2, Academic Press, New York 1964; The Aromatic Sextet, J. Wiley, London 1972.

[8] Cf. *R. McWeeny,* Proc. Phys. Soc., London, Ser. A **64,** 261, 921 (1951).
[9] *G. Ege* and *H. Vogler,* Theor. Chim. Acta **26,** 55 (1972).
[10] *C. W. Haigh, R. B. Mallion,* and *E. A. G. Armour,* Mol. Phys. **18,** 751 (1970), and further references given there.
[11] *C. F. Wilcox,* personal communication.
[12] *H. Vogler,* Tetrahedron Lett. **1979,** 229.
[13] For further details see *D. Schweitzer, K. H. Hausser, H. Vogler, F. Diederich,* and *H. A. Staab,* Mol. Phys. **46,** 1141 (1982).
[14] *E. Clar,* Polycyclic Hydrocarbons, Vol. 2, p. 97, Academic Press, New York 1964.
[15] *H. Vogler,* Mol. Phys. **43,** 83 (1981); see also *Chr. Bräuchle, H. Kabza,* and *J. Voitländer,* Chem. Phys. **48,** 369 (1980).

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