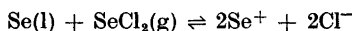


no indication that the vitreous carbon was attacked by the selenium melts, even in the presence of Cl.

Data with the new cell (Fig. 1) would hence be less influenced by impurities than our earlier data. Also, the correction for κ_0 is smaller. The data now give a slope of 1/4 for $\log \kappa$ versus $\log p(\text{SeCl}_2)$, which indicates that each SeCl_2 gives four charged particles. The simplest way of writing such a reaction is the following:



As usual for equilibrium data, it is not possible to say how many molecules of the solvent (Se) are attached to each particle. So the formulas might be written Se_n^+ and Se_nCl^- . This "chemical" picture can easily be seen to be equivalent to a "physical" picture of electron holes and of excess electrons, connected with Cl atoms. A certain electron hole need not necessarily stay with the same Se atom: on the contrary, a large part of the "mobility of Se^+ " may really be caused by jumps of an electron hole from one Se atom to another. Analogously the high apparent mobilities of H_3O^+ or OH^- in water are only to a small extent connected to the movement of the same H_3O^+ or OH^- particle but result from jumps of protons or proton holes between the water molecules.

The "chemical" picture has the advantage that it allows one, by traditional ways of thinking, to predict how κ will vary with $p(\text{SeCl}_2)$.

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The Molecular Structure of 1,3,5,7-Cyclo-octatetraene

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The molecular structures of 1,3-butadiene¹ and 1,3,5,7-cyclo-octatetraene² (COT) have previously been studied by the gas electron diffraction method. According to these investigations the carbon-carbon double bond distances were approximately the same in the two molecules, while the carbon-carbon single bond distance was found to be 0.021 Å larger for 1,3-butadiene than for COT. These results are hard to explain on the basis of p -electron delocalization. In view of the importance of the problem simultaneous reinvestigations of COT and 1,3-butadiene have therefore been carried through. The structural results for 1,3-butadiene are being published elsewhere³ while the parameters determined for COT are presented here.

The molecular structure of COT was determined by the sector electron diffraction method, using a modified s^3 sector. The intensity data were treated according to the usual procedure,⁴ yielding an $sM(s)$ -intensity function in the s -region from $s = 1.25 \text{ \AA}^{-1}$ to $s = 60 \text{ \AA}^{-1}$. The intensity data in the outer s -region ($s \geq 45 \text{ \AA}^{-1}$) were not too good and the outer s -limit was therefore set equal to 45 \AA^{-1} .

The carbon-carbon single and double bond distances were determined by applying auto- and cross-correlation functions⁵ to the intensity data, a method that is particularly well suited to determine closely spaced bond distances as they occur in the COT molecule.

The structural parameters for the molecule as a whole were determined by a least-squares refinement of the molecular intensity function. The results obtained from the least-squares adjustment are presented in Table 1. The numbering of the carbon atoms in the molecule is demonstrated in Fig. 1, which also shows the geometrical shape of the COT molecule. Fig. 2 shows the experimental molecular intensity function ($sM(s)$ -function) and the corresponding theoretical function calculated on the basis of the parameters presented in Table 1. The $sM(s)$ -functions shown in Fig. 2 were both multiplied with

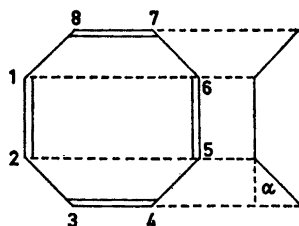


Fig. 1. 1,3,5,7-Cyclo-octatetraene. Model of the carbon framework which shows the numbering of the carbon atoms.

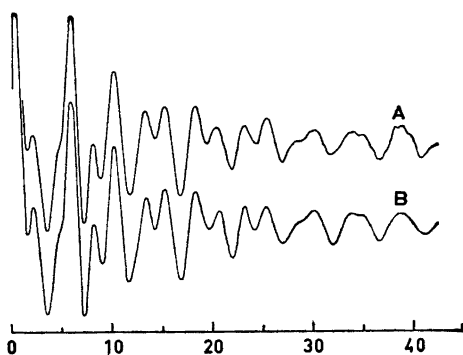


Fig. 2. Experimental (A) and theoretical (B) molecular intensity functions for 1,3,5,7-cyclo-octatetraene.

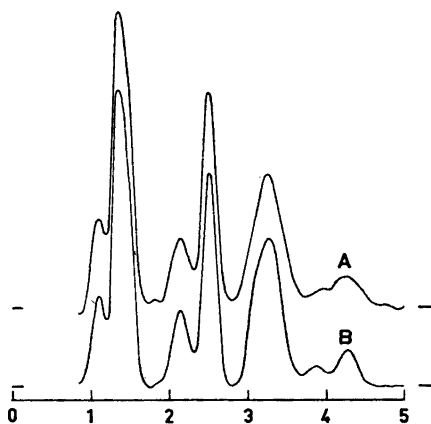


Fig. 3. Experimental (A) and theoretical (B) radial distribution functions for 1,3,5,7-cyclo-octatetraene.

Table 1. 1,3,5,7-Cyclo-octatetraene. Internuclear distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of a least-squares refinement of the molecular intensity data.

Distance	$r_g(1)$, Å	$\Delta r_g(1)$, Å	u , Å	Δu , Å
C=C	1.340 ₃	0.001 ₀	0.045 ₅	0.001 ₀
C-C	1.475 ₃	0.001 ₄	0.054 ₃	0.001 ₃
C ₁ C ₃	2.511 ₄	0.001 ₂	0.067 ₀	0.001 ₃
C ₁ C ₆	3.080 ₃		0.132 ₅	0.010 ₃
C ₁ C ₄	3.230 ₅		0.115 ₀	0.006 ₃
C ₁ C ₅	3.359 ₇		0.134 ₆	0.011 ₃
C-H	1.100 ₁	0.003 ₃	0.080 ₆	0.003 ₂

$$\angle \text{C}=\text{C}-\text{C}: 126.1_3^\circ \pm 0.5^\circ$$

$$\angle \text{H}-\text{C}=\text{C}: 117.6^\circ \pm 0.5^\circ$$

$$\angle \alpha: 43.1^\circ \pm 0.5^\circ$$

the damping function $\exp(-0.0009s^2)$ and Fig. 3 shows the Fourier transforms of the modified molecular intensity functions.

The carbon-carbon single and double bond distances of 1.476 Å and 1.340 Å determined for COT in the present investigation have to be compared with the corresponding bond distances of 1.467 Å and 1.344 Å determined simultaneously for 1,3-butadiene.³ The differences between the single bond distances and double bond distances in the two molecules are small, but as far as the differences are significant they show that there is a larger amount of p -electron delocalization in the planar 1,3-butadiene molecule than in the tub-shaped 1,3,5,7-cyclo-octatetraene molecule. These results are in accordance with the current ideas concerning the correspondence between π -orbital overlap and bond distance lengths.

A full account of the work will be published later together with a thorough discussion of the sp^2 - sp^2 carbon-carbon single bond length.

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The Molecular Structures of 1,3-Butadiene and 1,3,5-*trans*-Hexatriene

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The molecular structures of 1,3-butadiene and 1,3,5-*trans*-hexatriene in the vapour phase have been studied by the sector electron diffraction method, using a modified s^3 sector. The results presented in this work are parts of our endeavour to study the factors determining the lengths of sp^2 - sp^2 carbon-carbon single bonds. The research program also includes molecules like 1,3,5,7-cyclo-octatetraene,¹ 1,3,5-*cis*-hexatriene, 1,3-cyclo-pentadiene and the *cis,cis*-, *cis,trans*- and *trans,trans*-3,4-dimethyl-2,4-hexadienes.

The molecular structure of 1,3-butadiene reported here was determined simultaneously as the molecular structure of 1,3,5,7-cyclo-octatetraene reported elsewhere.¹ The two structures attract interest because of a reported discrepancy between the carbon-carbon single bond lengths^{4,5} which was not in accordance with the current ideas of π -electron delocalization.

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The intensity data were treated according to the usual well-established procedure,² and for both molecules the effective s -region of the resulting molecular intensity functions ($sM(s)$ -functions) extended from $s = 1.25 \text{ \AA}^{-1}$ to about $s = 45 \text{ \AA}^{-1}$. The bonded distances in the molecules were determined by applying auto- and cross-correlation functions³ to the intensity data, while the complete structures in both cases were determined by least-squares refinements of the molecular intensity functions. Tables 1 and 2 give the structural parameters obtained for 1,3-butadiene and 1,3,5-*trans*-hexatriene, respectively.

Table 1. 1,3-Butadiene. Internuclear distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of a least-squares refinement of the molecular intensity data.

Distance	$r_g(1), \text{ \AA}$	$\Delta r_g(1), \text{ \AA}$	$u, \text{ \AA}$	$\Delta u, \text{ \AA}$
C=C	1.343 ₉	0.000 ₅	0.043 ₆	0.000 ₅
C-C	1.467 ₂	0.001 ₃	0.051 ₃	0.001 ₀
C ₁ C ₃	2.469 ₅	0.001 ₃	0.064 ₆	0.001 ₂
C ₁ C ₄	3.698 ₁	0.003 ₄	0.059 ₁	0.002 ₇
C-H	1.094 ₄	0.001 ₃	0.082 ₁	0.001 ₁

$$\angle \text{C}=\text{C}-\text{C}: 122.8^\circ \pm 0.5^\circ$$

$$\angle \text{H}-\text{C}=\text{C}: 119.5^\circ \pm 1.0^\circ$$

Angle of rotation around C-C bond: 0.0°

Table 2. 1,3,5-*trans*-Hexatriene. Internuclear distances, root-mean-square amplitudes of vibrations, bond angles and standard deviations as results of a least-squares refinement of the molecular intensity data.

Distance	$r_g(1), \text{ \AA}$	$\Delta r_g(1), \text{ \AA}$	$u, \text{ \AA}$	$\Delta u, \text{ \AA}$
C=C	1.345 ₂	0.001 ₀	0.043 ₃	0.001 ₄
C-C	1.450 ₄	0.002 ₃	0.052 ₅	0.002 ₅
C ₁ C ₃	2.472 ₀	0.002 ₃	0.058 ₄	0.001 ₇
C ₁ C ₄	3.699 ₂	0.007 ₅	0.067 ₅	0.008 ₈
C ₂ C ₅	3.823 ₆	0.067 ₅	0.067 ₅	0.020 ₀
C ₁ C ₅	4.938 ₇	0.095 ₁	0.095 ₁	0.011 ₉
C ₁ C ₆	6.129 ₄	0.020 ₇	0.084 ₁	0.024 ₈
C-H	1.102 ₇	0.003 ₃	0.080 ₇	0.002 ₆

$$\angle \text{C}=\text{C}-\text{C}: 124.3^\circ \pm 1.5^\circ$$

$$\angle \text{H}-\text{C}=\text{C}: 117.8^\circ \pm 1.5^\circ$$