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An Electron Diffraction Study of the Structures of Thiophene, 2-Chlorothiophene and 2-Bromothiophene. A Note

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The conclusions from the electron diffraction study of Harshbarger & Bauer are discussed. It is thought that they have not established that the thiophene ring deviates from C_{2v} symmetry.

Introduction

In their investigation of the molecular structures of thiophene, 2-chlorothiophene and 2-bromothiophene, Harshbarger & Bauer (1970) (hereafter to be abbreviated to HB for convenience), made the attempt to establish whether the thiophene ring geometry is immutable upon substitution, as it must be assumed to be in benzene and *s*-triazene. To this end HB determined the structures of 2-chlorothiophene and 2-bromothiophene by gas-phase electron diffraction. They concluded that their investigation clearly shows that in these compounds the thiophene ring deviates from C_{2v} symmetry when halogen atoms are attached to the 2 position, and that, although their diffraction analyses did not distinguish between two slightly different molecular models, other physical and chemical evidence favoured one of these.

However, a careful comparison of these two models, *A* and *B*, and of the standard deviations of the geometry parameters (see Tables 1 and 2) suggests that a symmetric C_{2v} structure which is an 'average' of *A* and *B* or even a completely undistorted thiophene ring might also fit nicely in with the electron diffraction data, the

more so as the convergence difficulties involved in the greatly correlated parameter set in the unrestrained unsymmetrical refinement as described by HB, might decrease considerably by introducing parameter constraints *via* a symmetrical ring. At least, one could investigate quantitatively the significance of the unsymmetric ring used by HB in relation to a C_{2v} ring or a thiophene ring by least-squares refinements of all these structures, and subsequent comparison of residuals, standard deviations *etc.*

In this note the results of such a comparison are presented.

Results

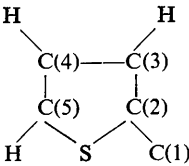
The HB procedure was followed as closely as possible (Bonham & Bartell, 1959). Their observed intensities were reproduced by careful reading of their photographically enlarged Figs. 5 and 7 for integral *q* values. This of course introduces additional, though small, random errors compared with HB's data. Scattering factors for Br were taken from Cromer, Larson & Waber's (1964) tables, and those for C, H, S and Cl from Hanson, Herman, Lea & Skillman's (1964) data. All refinements were carried out with our ALGOL-60

least-squares program *DERJ-ED01*, which closely resembles the FORTRAN program used by the Oslo Electron Diffraction group (Andersen, Seip, Strand & Stölevik, 1969). In the analyses one scale factor was refined. For distances involving hydrogen atoms an average vibrational amplitude was included.

For 2-chlorothiophene the results of the refinements are listed in Table 1, for 2-bromothiophene in Table 2. Our standard deviations are presented as they were delivered by the program, which means that they are probably highly underestimated (Seip, Strand & Stölevik, 1969). The final results of HB are reproduced in columns *A* and *B*. In column *C* the parameters for a C_{2v} ring structure are given, and in column *D* those for a C_{2v} ring with C(3)–C(4) restrained at the thiophene value. The structure of thiophene given by Bonham & Momany (1963), which we preferred to HB's because

of its better agreement with the microwave structure of Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen (1961) is listed in column *F*. In column *E* the parameters obtained by further refinement of HB's model *A* with 'our' observed intensity curve and all vibrational amplitudes fixed at HB's values are given. In our opinion the differences between these and HB's values cannot be due to the small differences in the observed intensities alone (when we refined only the scale factor for model *A* we found for 2-chlorothiophene: $R=0.147$; $\sum w\Delta^2=0.0262$; standard deviation $=0.0153$), but they must have been caused mainly by the enormous correlation of the parameters (for the model of column *C* for 2-chlorothiophene 6 correlation coefficients are higher than 0.8), which makes many of the parameters well-nigh undeterminable. For 2-bromothiophene the results of column *C* are parameters

Table 1. Comparison of structures obtained by least-squares fitting of 2-chlorothiophene data

Bond distances and angles						
	Model <i>A</i> of HB	Model <i>B</i> of HB	<i>C</i> C_{2v} ring	<i>D</i> C_{2v} ring 1 restraint	<i>E</i> Model <i>A</i> refined	<i>F</i> Thiophene (Bonham & Momany, 1963)
C(2)–S	1.727 (0.012) Å	1.709 (0.026) Å	1.713 (0.005) Å	1.718 (0.005) Å	1.706 (0.018) Å	1.714 (0.004) Å
C(5)–S	1.715 (0.012)	1.742 (0.012)	1.713	1.718	1.708	1.714
C(2)–C(3)	1.391 (0.016)	1.409 (0.016)	1.381 (0.006)	1.359 (0.003)	1.378 (0.013)	1.370 (0.006)
C(4)–C(5)	1.359 (0.010)	1.380 (0.034)	1.381	1.359	1.355 (0.010)	1.370
C(3)–C(4)	1.398	1.361	1.369 (0.012)	1.42*	1.402	1.419 (0.007)
C–H	1.073 (0.010)	1.077 (0.012)	1.090 (0.007)	1.088 (0.008)	1.083 (0.010)	1.092 (0.008)
C–Cl	1.713 (0.010)	1.706 (0.016)	1.709 (0.007)	1.701 (0.008)	1.722 (0.008)	
C—S—C	90.8 (0.3)°	91.2 (0.3)°	91.0 (0.3)°	91.2 (0.3)°	90.6 (0.2)°	92.2 (0.3)°
S—C(5)–C(4)	111.3 (0.6)	111.1 (0.6)	111.6	111.3	111.5 (0.4)	111.4 (0.2)
S—C(2)–C(3)	112.6 (0.8)	110.9 (1.4)	111.6	111.3	113.8 (0.6)	111.4
S—C—Cl	120.1 (0.6)	121.7 (0.8)	120.7 (0.2)	120.6 (0.3)	120.0 (0.8)	
C(2)–C(3)–H			107 (4)	115 (3)		
S—C(5)–H			101 (10)	95 (8)		
Amplitudes of vibration						
C–S	0.051 (0.008) Å	0.047 (0.004) Å	0.049 (0.001) Å	0.049 (0.001) Å	0.051 Å*	0.049 (0.005) Å
C–C	0.048 (0.004)	0.047 (0.004)	0.051 (0.002)	0.042 (0.002)	0.048*	0.046, 0.044*
C–H	0.065 (0.012)	0.065 (0.010)	0.053 (0.007)	0.055 (0.008)	0.065*	0.07 (0.01)
C–Cl	0.044 (0.014)	0.045 (0.006)	0.046 (0.004)	0.046 (0.004)	0.044*	
S...C	0.050 (0.004)	0.061 (0.004)	0.058 (0.002)	0.057 (0.002)	0.050*	
C...Cl	0.067 (0.004)	0.066 (0.006)	0.065 (0.002)	0.068 (0.002)	0.067*	
S...Cl	0.066 (0.004)	0.065 (0.004)	0.065	0.068	0.066*	
C...C	0.046 (0.008)	0.051 (0.006)	0.060 (0.006)	0.072 (0.011)	0.046*	
X...H			0.133 (0.027)	0.112 (0.029)	0.112*	
Scale factor			174.45 (2.90)	175.21 (3.19)	177.22 (2.53)	
Standard deviation	0.01724	0.01691	0.0112	0.0122	0.0113	
$\sum w\Delta^2$	0.02936	0.02711	0.0119	0.0144	0.0129	
$\sum I_{obs} $			10.26	10.22	10.11	
R^\dagger			0.096	0.105	0.103	
Number of parameters	11 or 9	11 or 9	18	17	11	

* These parameters are not refined

† R is defined as $\sum |\Delta| / \sum |I_{obs}|$ where $\Delta = I_{obs} - I_{calc}$.

for a subsidiary minimum of $\sum w\Delta^2$. Column *D* indicates that there must be a better structure which is not found here, probably because of too inaccurate start-parameters.

Discussion

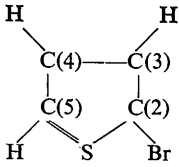
It is found for both 2-chlorothiophene and 2-bromothiophene that the goodness of fit between calculated and observed data for the C_{2v} ring structure and even for the thiophene-like ring of column *D* is comparable to that for the unsymmetric structures of HB. For 2-bromothiophene the overall fit is far worse than for 2-chlorothiophene. The standard deviations for both compounds are of equal magnitude, but not so the relative standard deviations.

In all refinements the parameters are closely correlated, even to such a degree that for unsymmetric struc-

tures it is impossible to refine geometric parameters and vibrational amplitudes simultaneously. An alternating refinement of both types of parameters of course may give a least-squares solution, but there is no guarantee that this is the 'true' structure. If one fixes a set of vibrational amplitudes, the geometric parameters refine to the best value for it, and a subsequent refinement of the vibrational amplitudes alone will not remove this dependence. In such a case one has to conclude that it is impossible to determine the geometry. A solution for this convergence problem might be the introduction of constraints in geometrical and/or vibrational parameters, or rather a calculation of the vibrational amplitudes from spectroscopical data, and introduction of these values as 'true' values in the electron-diffraction least-squares refinement.

We conclude that for 2-chlorothiophene and 2-bro-

Table 2. Comparison of structures obtained by least-squares fitting of 2-bromothiophene data

Bond distances and angles						
	Model <i>A</i> of HB	Model <i>B</i> of HB	<i>C</i> C_{2v} ring	<i>D</i> C_{2v} ring 1 restraint	<i>E</i> Model <i>A</i> refined	<i>F</i> Thiophene (Bonham & Moman, 1963)
C(2)–S	1.744 (0.008) Å	1.668 (0.008) Å	1.704 (0.003) Å	1.703 (0.003) Å	1.736 (0.005) Å	1.714 (0.004) Å
C(5)–S	1.668 (0.008)	1.740 (0.008)	1.704	1.703	1.672 (0.005)	1.714
C(2)–C(3)	1.390 (0.014)	1.465 (0.016)	1.365 (0.005)	1.383 (0.005)	1.385 (0.009)	1.370 (0.006)
C(4)–C(5)	1.341 (0.014)	1.339 (0.016)	1.365	1.383	1.343 (0.009)	1.370
C(3)–C(4)	1.464	1.393	1.455 (0.013)	1.42*	1.465	1.419
C–H	1.091 (0.026)	1.089 (0.030)	1.078 (0.017)	1.093 (0.014)	1.100 (0.018)	1.092 (0.008)
C–Br	1.849 (0.008)	1.850 (0.008)	1.866 (0.005)	1.865 (0.004)	1.857 (0.005)	
C—S—C	92.0 (0.6)°	92.8 (0.8)°	91.9 (0.4)°	92.3 (0.4)°	91.9 (0.4)°	92.2 (0.3)°
S—C(5)—C(4)	114.7 (1.2)	111.1 (1.4)	112.7	111.8	114.3 (0.9)	111.4 (0.2)
S—C(2)—C(3)	110.9 (1.0)	111.1 (1.0)	112.7	111.8	111.4 (0.7)	111.4
S—C—Br	120.7 (0.6)	125.2 (0.8)	121.5 (0.6)	122.5 (0.4)	120.6 (0.5)	
C(2)–C(3)–H			120 (2)	130 (6)		
S—C(5)–H			117 (7)	126 (13)		
Amplitudes of vibration						
C–S	0.047 (0.006) Å	0.047 (0.006) Å	0.059 (0.005) Å	0.060 (0.004) Å	0.047* Å	0.049 (0.005) Å
C–C	0.047 (0.010)	0.043 (0.010)	0.061 (0.009)	0.072 (0.005)	0.046*	0.046, 0.044*
C–H	0.080 (0.030)	0.080 (0.030)	0.081 (0.024)	0.085 (0.023)	0.080*	0.07 (0.01)
C–Br	0.047 (0.006)	0.047 (0.006)	0.041 (0.015)	0.044 (0.012)	0.047*	
S···C	0.050*	0.050 (0.006)	0.052 (0.006)	0.057 (0.005)	0.050*	
C···Br	0.105 (0.012)	0.078 (0.016)	0.130 (0.014)	0.129 (0.013)	0.105*	
S···Br	0.078 (0.004)	0.075 (0.004)	0.088 (0.005)	0.090 (0.004)	0.078*	
C···C	0.050*	0.041 (0.012)	0.040 (0.015)	0.061 (0.015)	0.050*	
X···X			0.086 (0.026)	0.041 (0.023)	0.100*	
Scale factor			227.7 (8.9)	228.9 (7.8)	211.5 (5.7)	
Standard deviation	0.01578	0.01563	0.0125	0.0112	0.0115	
$\sum w\Delta^2$	0.02804	0.02703	0.0149	0.0119	0.0136	
$\sum I_{\text{obs}} $			4.25	4.22	4.57	
R^\dagger			0.24	0.21	0.21	
Number of parameters	11 or 7	11 or 9	19	18	11	

* These parameters are not refined.

† R is defined as $\sum |A|/\sum |I_{\text{obs}}|$, where $A = I_{\text{obs}} - I_{\text{calc}}$.

mothiophene it is impossible to derive from the electron diffraction data whether the thiophene ring deviates from C_{2v} -symmetry or is distorted at all upon halogen substitution.

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The Crystal and Molecular Structure of *cis*-Dichloro(*meso*-2,3-diaminobutane)palladium(II)

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The crystal and molecular structure of *cis*-dichloro(*meso*-2,3-diaminobutane)palladium(II), $[\text{PdCl}_2(\text{C}_4\text{H}_{12}\text{N}_2)]$, has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group $Pbca$ with eight molecules in a unit cell of dimensions $a = 10.072$, $b = 16.093$ and $c = 10.932$ Å. The structure was refined by block-diagonal least-squares methods using 1628 independent reflexions to give $R = 0.038$. The complex molecule has square-planar coordination. Two chlorine atoms are in *cis* positions with Pd-Cl distances of 2.316 and 2.318 Å. The five-membered chelate ring is puckered. One of the two substituted methyl groups is equatorial with respect to the chelate ring, whereas the other is axial. The molecule is dissymmetric and two enantiomeric molecules exist in the crystal. Each enantiomer is linked by a N-H...Cl hydrogen bond to form a chain parallel to the c axis. These chains are also bound laterally by N-H...Cl bonds. Thus the molecules make up a two-dimensional network parallel to the plane (010). The Pd-Pd distance is 3.34 Å, suggesting a weak interaction between the d orbitals.

Introduction

meso-2,3-Diaminobutane usually coordinates to a metal atom to form a puckered chelate ring. Consequently one of the two C-CH₃ bonds will be in the equatorial position with respect to the chelate ring, whereas the other will be in the axial position. The nuclear magnetic resonance spectra of the Pt(II) or Co(III) complex containing this ligand in heavy water show only one signal corresponding to the methyl group, suggesting a puckering motion of the chelate ring in solution (Yano, Ito, Koike, Fujita & Saito, 1969). The structure determination of *cis*-dichloro(*meso*-2,3-diaminobutane)palladium(II) has been undertaken to obtain structural details of the chelate ring in crystals, since the crystals of this palladium analogue are extremely suitable for X-ray analysis.

However, the crystals were sparingly soluble in water and measurement of nuclear magnetic resonance was unsuccessful.

Experimental

A sample of the complex was kindly supplied by Dr H. Ito and Professor K. Saito of Tohoku University. Suitable crystals were grown by slow evaporation of an aqueous solution. Preliminary oscillation and Weissenberg photographs showed that the crystals are orthorhombic with systematic absences given by $0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$. These absences are consistent with the space group $Pbca$ (No. 61). A specimen for intensity measurements was selected from the recrystallized sample without further treatment; the crystal was approximately cubic (about 0.2 mm in dimension). The intensity data were meas-