Les atomes de rubidium se répartissent autour de l'ion bicondensé à une distance variant de 4,08 à 4,78 Å de l'atome d'uranium. Les plus proches voisins des atomes de rubidium sont trois atomes de fluor et un atome d'oxygène à une distance moyenne de 2,80 Å.

Les structures de $Rb_2UO_2F_4.H_2O$ et $Cs_2UO_2F_4.H_2O$ présentent des analogies mais elles ne sont pas isotypes.

Références

DAVIDOVICH, R. L., SERGIENKO, V. I. & KALACHEVA, T. A. (1968). *Izv. Akad. Nauk SSSR, Ser. Khim*, **8**, 1678.

NGUYEN QUY DAO (1972). *Acta Cryst.* Sous presse.

SERGIENKO, V. I. & DAVIDOVICH, R. L. (1970). *Spectrosc. Letters*, **3**, 35.

Acta Cryst. (1972). B**28**, 2619

On the structures of 2-chlorothiophene and 2-bromothiophene.

By R. R. KARL and S. H. BAUER, *Department of Chemistry, Cornell University, Ithaca, New York* 14850, *U.S.A.*

(*Received* 4 *January* 1972 *and in revised form* 28 *March* 1972)

The original electron diffraction data for the monohalothiophenes (2 position) were reanalyzed, following currently improved procedures. It was again demonstrated that models with undistorted C_4H_4S rings do not fit the scattered intensity functions as well as do the initially proposed models (*A* or *B*), in contrast to conclusions published by Derissen, Kocken and van Weelden.

In a recently published note, Derissen, Kocken & van Weelden (1971) (DKW) reported their reanalysis of our electron diffraction data on the halosubstituted thiophenes, and concluded that structures in which the ring conformed to C_{2v} symmetry are in as good agreement with our molecular scattering intensities as are the initially proposed structures, *A* and *B*. DKW obtained their intensity functions by careful reading of photographic enlargements of our Figs. 5 and 7 (Harshbarger & Bauer, 1970). Such a procedure is highly suspect since it introduces correlations between adjacent points and incorporates a sequence of optical distortions, as well as the assumption that the draftsman was meticulous in reproducing our plotted curves (which were never intended to be a basis for precise data reporting). Indeed, the very low standard deviations they found strongly suggest the presence of large correlations rather than demonstrate an optimum fit of their model. Our original data are on file and will be sent to anyone on request. We consider the procedure followed by DKW to be erroneous and the acceptance of their note prior to submitting it to the original authors for comments to be an oversight by the journal.

It is well known, and it was clearly pointed out in our paper (Harshbarger & Bauer, 1970), that the one-dimensional Fourier transforms derived from gas diffraction data do not necessarily lead to unique molecular structures. For these compounds configurations *A* and *B* fit the molecular scattered intensity functions equally well and the choice must be made on the basis of other information. The question remains whether undistorted ring models or distorted ones are in 'best agreement' with the precise data, subject to certain constraints. In addition to criteria for adequacy of fit between observed and calculated intensities, to within some specified statistical limits, the final distances, bond angles, and root-mean-square amplitudes must fall within acceptable ranges. The symmetric ring structures proposed by DKW fail to meet the latter test. From our tabulated data for the C_{2v} model, values of l(S–C) and l(C–C)'s range from 0·059–0·066 Å for the bromocompound, which are too large for such a well-knit structure. In contrast, the distorted models lead to corresponding values (0·045–0·051 Å), in agreement with magnitudes we found for the unsubstituted thiophene. The latter check the values reported by Bonham & Momany (1963), and agree with the calculated spectroscopic estimates by Cyvin, Cyvin, Hagen & Markov (1969). The C_{2v} constraint on chlorothiophene gave unacceptably large bond angles at C(4)C(3)H and C(4)C(5)H (> 140°), and correspondingly small angles at SC(5)H and C(2)C(3)H (< 110°). Finally, in their remarks regarding the structure of the unsubstituted thiophene DKW implied that the parameters reported by us, derived from two sets of data covering the range $6 < q < 125$, were less acceptable than those reported by Bonham & Momany (1963) which covered the smaller data range $15 < q < 90$, because the latter parameters were in slightly better agreement with the microwave structure reported by Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen (1961). DKW failed to recognize that the microwave parameters are r_s values and should not be confused with electron diffraction parameters (r_a); the former are often 0·01 Å smaller than the latter due to the difference in the inherent averaging process by these two structural probes.

To substantiate our response to DKW we undertook a reanalysis of our tabulated data following current techniques, which we believe are superior to those available in 1968 when our previous reduction was completed. The principal innovations are a less subjective manner for drawing in the background function and ease of search for satisfactory structures. Thus, for each model we now have two sets of $qM(q)$ values, the original intensities with Harshbarger's background and the same intensities with Karl's background. It is worth noting that the tabulated data were obtained by averaging over a minimum of three plates for each range in scattering angles, while each plate was scanned several times. Between three to four times as many points were recorded as integral q values used. The standard deviations in measured densities among multiple recordings are generally 0·8%, and always less than 1·2%. At any one radial position in the diffraction pattern the polar averaged photometric precision is such that for ten readings the standard deviation is between 3 to 5 parts per 10,000. Discussions of both the random and systematic errors applicable to our operations are given in HB's paper and in other publications from this laboratory (Oberhammer & Bauer, 1969; Hilderbrandt & Bauer, 1969). Analytic expansions for the Forsyth & Wells (1959) atomic scattering factors were first used, as initially programmed; later, the results were checked using the Tavard, Nicholas & Rouault (1967) form factors. The *A* models of HB require *thirteen* independent structural parameters. For the 33 distinct atom-pair separations we assigned (as did HB) *twenty* independent root-mean-square amplitudes. The undistorted ring models (C_{2v}) are specified by *nine* structural parameters and for these 26 atom-pair distances *nine* independent l_{ij}'s were inserted. Eight least-squares calculations were made for each compound, using the $I(q)$ values from our files. In these all the structural parameters were varied simultaneously.

I: DKW (C_{2v}), structure as published by Derissen *et al.*, 1971); HB's background (two sets of form factors).
II: Model *A*, as published by Harshbarger & Bauer (1970); HB's background.
III: C_{2v} structure, KB's optimized background. A new least-squares reduction of $qM(q)$.
IV: *M*odel *A*, KB's optimized background. A new least-squares reduction of $qM(q)$.

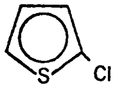
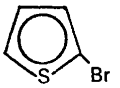
Inspection of Table 1 shows that the σ's and the *R*'s for (I) are greater than those for all other combinations, irrespective of the form factors inserted. To apply statistical tests note that 115 data points were used to develop estimates for 18 parameters, needed to specify the C_{2v} models, and for 33 parameters needed to specify the *A* models. Let us now calculate Hamilton's *R* value ratio (Hamilton, 1965). To achieve a 99·5% confidence level for the improved model, with $(m–m) = 115–33$ = No. of degrees of freedom; $b = 33–18$ = dimension of hypothesis, $\mathscr{R}_{15,82,0\cdot005} = 1\cdot212$. From Table 1 for the chloro compound, $\mathscr{R}(\mathrm{III/IV}) = 1\cdot24$, and $\mathscr{R}(\mathrm{I/IV}) = 2\cdot91$; the corresponding values for the bromo substituted compound are: $\mathscr{R}(\mathrm{III/IV}) = 1\cdot45$ and $\mathscr{R}(\mathrm{I/IV}) = 1\cdot91$. Thus, the tabulated data show that all C_{2v} constrained structures are clearly rejected at the 99·5% confidence level.* For the new backgrounds there still is a significant margin for the *A* structure over the C_{2v} model for the bromo com-

---

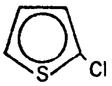
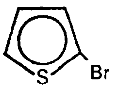
* Note that the Student *t*-test (Kreysig, 1965) also rejects the C_{2v} structures at the 99.5% level.

Table 1. *Standard deviations and R values for various models, using original scattering data*

Forsyth and Wells (coherent) and Bewilogua (incoherent)

		I	II	III	IV
	σ	0·0369	0·0244	0·0180	0·0158
	R	0·1643	0·1015	0·0856	0·0751
	σ	0·0237	0·0189	0·0160	0·0136
	R	0·2458	0·1989	0·1630	0·1347

Tavard (coherent) and Bewilogua (incoherent)

		I	II	III	IV
	σ	0·0435	0·0276	0·0185	0·0161
	R	0·1732	0·1144	0·0739	0·0596
	σ	0·0243	0·0233	0·0167	0·0139
	R	0·2233	0·1998	0·1699	0·1171

$$\sigma = \left[\frac{\sum(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2}{N_{\mathrm{pts}}}\right]^{1/2}; \quad R = \frac{\sum|I_{\mathrm{obs}} - I_{\mathrm{calc}}|}{\sum I_{\mathrm{obs}}}$$

Table 2. 2-*Chlorothiophene: parameters and* l_{ij}*'s*

Parameters	DKW	II	III	IV
C(2)–S	1·713 (15)	1·727 (14)	1·718 (8)	1·722 (4)
C(5)–S	1·713 (15)	1·715 (14)	1·718 (8)	1·717 (5)
C(2)–C(3)	1·381 (18)	1·391 (21)	1·382 (13)	1·389 (11)
C(4)–C(5)	1·381 (18)	1·359 (13)	1·382 (13)	1·378 (9)
C(3)–C(4)	1·369 (36)	1·398*	1·398*	1·392*
C–H	1·090 (21)	1·073 (13)	1·085 (15)	1·071 (10)
C–Cl	1·709 (21)	1·713 (13)	1·707 (12)	1·713 (4)
C–S–C	91·0 (0·9)	90·8 (0·4)	90·8 (0·3)	91·0 (0·2)
∠S–C(5)–C(4)	111·6*	111·3 (1·1)	112·0 (0·8)	111·0 (0·4)
∠S–C(2)–C(3)	111·6*	112·6 (1·1)	112·0 (0·8)	112·9 (0·3)
∠S–C–Cl	120·7 (0·6)	120·1 (0·8)	120·9 (0·4)	120·2 (0·4)
∠C(2)–C(3)–H	107·0 (12)	128·0*	115·6 (25)	127·7*
∠C(5)–C(4)–H	107·0 (12)	126·0*	115·6 (25)	126·2*
∠C(4)–C(3)–H	140·1*	118·0†	131·8*	120·4 (4)
∠C(3)–C(4)–H	140·1*	118·0†	131·8*	120·4 (4)
∠S–C(5)–H	101·0 (30)	120·0†	104·9 (9)	117·0 (5)
∠C(5)–C(5)–H	147·4*	128·7*	143·1*	132·0*
l_{ij}'s				
C–S	0·049 (3)	00·051 (11)	0·045 (12)	0·050 (12)
C–C	0·051 (6)	0·048 (5)	0·048 (4)	0·049 (14)
C–H	0·053 (21)	0·065 (14)	0·049 (15)	0·066 (17)
C–Cl	0·046 (16)	0·044 (19)	0·040 (24)	0·044 (20)
S···C	0·058 (6)	0·050 (9)	0·051 (5)	0·050 (6)
C···Cl	0·065 (6)	0·067 (5)	0·070 (11)	0·068 (9)
S···Cl	0·065	0·066 (5)	0·063 (4)	0·063 (4)
C···C	0·060 (18)	0·046 (11)	0·047 (10)	0·047 (13)
X···H	0·133 (81)	0·08 to 0·12	0·07 to 0·14	0·08 to 0·13

* Derived from varied parameters.
† Constrained during least-squares refinement. Numbers in parenthesis are 3σ.

Table 3. 2-*Bromothiophene: parameters and* l_{ij}*'s*

Parameters	DKW	II	III	IV
C(2)–S	1·704 (9)	1·744 (11)	1·703 (6)	1·749 (8)
C(5)–S	1·704 (9)	1·668 (11)	1·703 (6)	1·668 (9)
C(2)–C(3)	1·365 (15)	1·390 (14)	1·373 (9)	1·384 (15)
C(4)–C(5)	1·365 (15)	1·341 (14)	1·373 (9)	1·338 (16)
C(3)–C(4)	1·455 (39)	1·464*	1·466*	1·466*
C–H	1·078 (51)	1·091 (35)	1·075 (33)	1·082 (33)
C–Br	1·866 (15)	1·849 (11)	1·855 (6)	1·845 (8)
∠C–S–C	91·9 (1·2)	92·0 (0·8)	92·3 (0·3)	91·6 (0·5)
∠S–C(5)–C(4)	112·7*	114·7 (1·4)	112·7 (0·5)	115·2 (1·1)
∠S–C(2)–C(3)	112·7*	110·9 (1·3)	112·7 (0·5)	110·7 (1·0)
∠S–C–Br	121·5 (1·8)	120·7 (0·8)	122·1 (0·8)	120·5 (0·5)
∠C(2)–C(3)–H	120·0 (6·0)	130·0*	133·6 (7)	129·8*
∠C(5)–C(4)–H	120·0 (6·0)	128·0*	133·6 (7)	128·1*
∠C(4)–C(3)–H	128·7*	120·0†	114·7*	121·1 (9)
∠C(3)–C(4)–H	128·7*	120·0†	114·7*	117·7 (9)
∠S–C(5)–H	117·0 (21)	121·0†	104·0 (10)	118·6 (7)
∠C(4)–C(5)–H	118·5*	124·3*	143·3*	126·2*
l_{ij}'s				
C–S	0·059 (15)	0·047 (8)	0·056 (7)	0·050 (9)
C–C	0·061 (27)	0·046 (13)	0·066 (9)	0·047 (12)
C–H	0·081 (72)	0·080 (4)	0·068 (33)	0·080 (27)
C–Br	0·041 (45)	0·047 (8)	0·039 (19)	0·046 (15)
S···C	0·052 (18)	0·050†	0·046 (7)	0·053 (12)
C···Br	0·130 (43)	0·105 (15)	0·068 (21)	0·099 (23)
S···Br	0·088 (15)	0·078 (5)	0·068 (6)	0·083 (9)
C···C	0·040 (15)	0·050†	0·039 (20)	0·058 (18)
X···H	0·086 (78)	0·08 to 0·12	0·07 to 0·87	0·08 to 0·13

* Derived from varied parameters.

† Constrained during least-squares refinement. Numbers in parenthesis are 3σ.

pound, but the difference between the III and IV cases for the chloro compound are within the assigned error limits (3σ). (Note that $\pm 3\sigma$ is 99·75% confidence level.) For the latter, therefore, the argument in favor of a distorted ring is not so strong but nonetheless is preferred on the basis of analogy; the C_{2v} structures do require the assignment of several exceptionally large valence angles. Further indication for the presence of distortion is the manner in which the least-squares program converged. By the way of contrast, when model *A* was assigned to thiophene the least-squares computation converged to very nearly a C_{2v} structure, even though the larger number of parameters was available to the program. However, the same model for the substituted compounds converged to a clearly distorted structure. In other words, the distortions derived from the least-squares analyses are not artifacts introduced by the procedure for optimizing the fitting of the diffraction data.

Comparison of the structural parameters and root-mean-square amplitudes for the various reductions are presented in Table 2 for the chloro and in Table 3 for the bromo compound. The refined backgrounds lead to minor changes in the magnitude of parameters and to a somewhat better fit between the calculated and the observed intensity functions. The effect of halogen for hydrogen atom substitution on the thiophene ring is not trivial for the bromo compound but is barely discernible for the chloro compound. This must be kept in mind when one introduces such substitutions to provide phase information in crystal structure analyses.

References

BAK, B., CHRISTENSEN, D., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1961). *J. Mol. Spectrosc.* 7, 58.

BONHAM, R. A. & MOMANY, F. A. (1963). *J. Phys. Chem.* **67**, 2474.

CYVIN, S. V., CYVIN, B. N., HAGEN, G. & MARKOV, P. (1969). *Acta Chem. Scand.* **23**, 3407.

DERISSEN, J. L., KOCKEN, J. W. M. & VAN WEELDEN, R. H. (1971). *Acta Cryst.* B**27**, 1692.

FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.

HARSHBARGER, W. R. & BAUER, S. H. (1970). *Acta Cryst.* B**26**, 1010.

HILDERBRANDT, R. L. & BAUER, S. H. (1969). *J. Mol. Struc.* **3**, 325.

KREYSIG, E. (1965). *Advanced Engineering Mathematics*, pp. 792–795. New York: John Wiley.

OBERHAMMER, H. & BAUER, S. H. (1969). *J. Amer. Chem. Soc.* **91**, 10.

TAVARD, C., NICHOLAS, D. & ROUAULT, M. (1967). *J. Chim. Phys.* **64**, 540.