

References

- BRADLEY, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
 COX, E. G., PINKARD, F. W., WARDLAW, W. & WEBSTER, K. C. (1935). *J. Chem. Soc.* p. 459.
 GROTH, P. (1968). *Acta Chem. Scand.* **22** (1), 128.
 LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951.
 MERRITT, L. L., GUARE, C. & LESSOR, A. E. (1956). *Acta Cryst.* **9**, 253.
 PFLUGER, C. E. (1958). Ph. D. Dissertation, Univ. of Texas, Austin, Texas.
 SRIVASTAVA, R. C., LINGAFELTER, E. C. & JAIN, P. C. (1967). *Acta Cryst.* **22**, 922.

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A refinement of the crystal structure of β -isoprene sulfone. By RONALD BEALL, JOHN K. HERDKLOTZ and RONALD L. SASS, *Department of Chemistry, William Marsh Rice University, Houston, Texas, U.S.A.*

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The crystal structure of β -isoprene sulfone, determined by Cox & Jeffrey and refined by Jeffrey has been re-refined. The crystals are monoclinic ($P2_1/m$) with $a=6.709$ (5), $b=7.67$ (1), $c=6.707$ (5) Å, $\beta=110.266$ (6)°, $Z=4$. Three-dimensional counter data were collected using silicon monochromatized Mo $K\alpha$ radiation. The structure was refined by full-matrix least squares to an R index of 0.069.

Introduction

The crystal structure of β -isoprene sulfone [Fig. 1(a)] was first determined by Cox & Jeffrey (1942) and later refined by Jeffrey (1951) using Fourier methods and the original data. Jeffrey (1951) reported the C(2)–C(3) bond length to be 1.37 (2) Å. This is considerably longer than one would expect for a carbon–carbon double bond. A related compound, butadiene [Fig. 1(b)] has been studied by Sands & Day

(1967) and they report the C(2)–C(3) bond length to be 1.299 (8) Å. As part of a study of cyclic sulfones in our laboratory we also have determined the structure of butadiene sulfone. Our results confirm those of Sands & Day. Because of this discrepancy in the C(2)–C(3) bond length between the two compounds, we have collected a set of three-dimensional data and have re-refined the structure of β -isoprene sulfone by full-matrix least squares.

Table 1. *Final atomic parameters and their e.s.d.'s*

The values in the Table have been multiplied by 10^4 .

The temperature factors are of the form: $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	2621 (2)	2500	298 (2)	146 (3)	103 (2)	159 (3)	0	55 (3)	0
C(1)	1140 (7)	2500	2097 (7)	154 (15)	145 (9)	237 (17)	0	108 (14)	0
C(2)	2866 (10)	2500	4218 (8)	383 (24)	213 (11)	155 (19)	0	135 (17)	0
C(3)	4860 (8)	2500	4362 (7)	260 (18)	106 (9)	188 (17)	0	-17 (15)	0
C(4)	5267 (7)	2500	2297 (8)	109 (15)	173 (10)	273 (20)	0	12 (14)	0
C(5)	6732 (15)	2500	6356 (11)	443 (34)	283 (20)	315 (31)	0	-122 (23)	0
O	2266 (3)	912 (3)	-0871 (3)	237 (7)	170 (5)	273 (9)	-13 (5)	96 (7)	-68 (5)
B									
H(1)	180 (38)	1522 (33)	2063 (40)	6.0					
H(2)	2413 (64)	2500	5037 (58)	6.0					
H(3)	5950 (39)	1448 (32)	2300 (42)	6.0					
H(4)	6395 (83)	2500	7247 (70)	6.0					
H(5)	7426 (44)	1661 (34)	6126 (45)	6.0					

Table 2. *A comparison of the bond distances and angles of β -isoprene and butadiene sulfone*

I		II	
S—O	1.424 (2) Å	S—O	1.440 (4) Å
S—C(1)	1.809 (6)	S—C(1)	1.795 (6)
S—C(4)	1.816 (4)	S—C(4)	1.792 (7)
C(1)–C(2)	1.491 (6)	C(1)–C(2)	1.475 (9)
C(2)–C(3)	1.307 (9)	C(2)–C(3)	1.299 (8)
C(3)–C(4)	1.501 (8)	C(3)–C(4)	1.482 (8)
C(3)–C(5)	1.482 (8)		

Table 2 (cont.)

O—S—O	117.6 (2)°	O—S—O	117.0 (3)°
C(1)—S—C(4)	97.5 (2)	C(1)—S—C(4)	97.0 (3)
O—S—C(1)	110.0 (1)	O—S—C(1)	110.3 (2)
O—S—C(4)	109.9 (1)	O—S—C(4)	110.2 (2)
S—C(1)—C(2)	102.2 (4)	S—C(1)—C(2)	104.2 (4)
S—C(4)—C(3)	103.7 (4)	S—C(4)—C(3)	102.8 (4)
C(1)—C(2)—C(3)	120.5 (5)	C(1)—C(2)—C(3)	116.8 (6)
C(2)—C(3)—C(4)	116.1 (4)	C(2)—C(3)—C(4)	119.3 (6)
C(2)—C(3)—C(5)	126.2 (6)		
C(4)—C(3)—C(5)	117.6 (6)		

I. β -Isoprene sulfone (This paper).

II. Butadiene sulfone (Sands & Day, 1967).

Experimental

Crystals of β -isoprene sulfone suitable for diffraction study were obtained by slow evaporation of an ethanol solution.

Table 3. Observed and calculated structure factors ($\times 10$) with those rejected by statistical criteria indicated by an asterisk

h	k	l	F _o	F _c	Rejection
0	0	0	100	100	
0	0	1	100	100	
0	0	2	100	100	
0	0	3	100	100	
0	0	4	100	100	
0	0	5	100	100	
0	0	6	100	100	
0	0	7	100	100	
0	0	8	100	100	
0	0	9	100	100	
0	0	10	100	100	
0	0	11	100	100	
0	0	12	100	100	
0	0	13	100	100	
0	0	14	100	100	
0	0	15	100	100	
0	0	16	100	100	
0	0	17	100	100	
0	0	18	100	100	
0	0	19	100	100	
0	0	20	100	100	
0	0	21	100	100	
0	0	22	100	100	
0	0	23	100	100	
0	0	24	100	100	
0	0	25	100	100	
0	0	26	100	100	
0	0	27	100	100	
0	0	28	100	100	
0	0	29	100	100	
0	0	30	100	100	
0	0	31	100	100	
0	0	32	100	100	
0	0	33	100	100	
0	0	34	100	100	
0	0	35	100	100	
0	0	36	100	100	
0	0	37	100	100	
0	0	38	100	100	
0	0	39	100	100	
0	0	40	100	100	
0	0	41	100	100	
0	0	42	100	100	
0	0	43	100	100	
0	0	44	100	100	
0	0	45	100	100	
0	0	46	100	100	
0	0	47	100	100	
0	0	48	100	100	
0	0	49	100	100	
0	0	50	100	100	
0	0	51	100	100	
0	0	52	100	100	
0	0	53	100	100	
0	0	54	100	100	
0	0	55	100	100	
0	0	56	100	100	
0	0	57	100	100	
0	0	58	100	100	
0	0	59	100	100	
0	0	60	100	100	
0	0	61	100	100	
0	0	62	100	100	
0	0	63	100	100	
0	0	64	100	100	
0	0	65	100	100	
0	0	66	100	100	
0	0	67	100	100	
0	0	68	100	100	
0	0	69	100	100	
0	0	70	100	100	
0	0	71	100	100	
0	0	72	100	100	
0	0	73	100	100	
0	0	74	100	100	
0	0	75	100	100	
0	0	76	100	100	
0	0	77	100	100	
0	0	78	100	100	
0	0	79	100	100	
0	0	80	100	100	
0	0	81	100	100	
0	0	82	100	100	
0	0	83	100	100	
0	0	84	100	100	
0	0	85	100	100	
0	0	86	100	100	
0	0	87	100	100	
0	0	88	100	100	
0	0	89	100	100	
0	0	90	100	100	
0	0	91	100	100	
0	0	92	100	100	
0	0	93	100	100	
0	0	94	100	100	
0	0	95	100	100	
0	0	96	100	100	
0	0	97	100	100	
0	0	98	100	100	
0	0	99	100	100	
0	0	100	100	100	

The crystal used in this study was prismatic in habit with an average diameter of 0.2 mm. The results of cell constant measurements and their estimated standard deviations are $a=6.709$ (5), $b=7.67$ (1), $c=6.707$ (5) Å, $\beta=110.266$ (6)°. The space group $P2_1/m$, rather than $P2_1$, was chosen on the basis of intensity statistics. Attempts to refine in the space group $P2_1$ confirmed this choice. A total of 1139 independent reflections were collected on a PAILRED diffractometer employing equi-inclination geometry. All data were collected using silicon-monochromatized Mo $K\alpha$ radiation. The fixed-counter moving-crystal method was used employing a 2° scan range and a 1° per minute scan speed. Background was measured for a fixed time of 2 minutes at the beginning and end of each scan. A total of 351 reflections were rejected on the basis that their counting statistical error (Ladell, 1965) exceeded 50% of the measured intensity. The intensity data were corrected for Lorentz and polarization factors (Bond, 1959). The maximum value of μR was 0.04 and no absorption corrections were made.

The starting coordinates used for the refinement were those reported by Jeffrey (1951). The refinement was carried out using the full-matrix least-squares program of *X-ray 63* (Stewart, 1964). The quantity minimized was $\sum w(F_o - F_c)^2$, where $w=1/\sigma^2$ and $\sigma^2=\frac{1}{4}[A(1+b)/(1-b)]$ where A is the geometric factor applied to the measured intensities and b equals the total background divided by the total number of counts (Evans, 1961). All hydrogen atoms were located in a difference map and included in the final refinement. The scattering factors used in the calculations were those of Doyle & Turner (1968) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms. The R index was lowered to a final value of 0.069 with use of individual anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature fac-

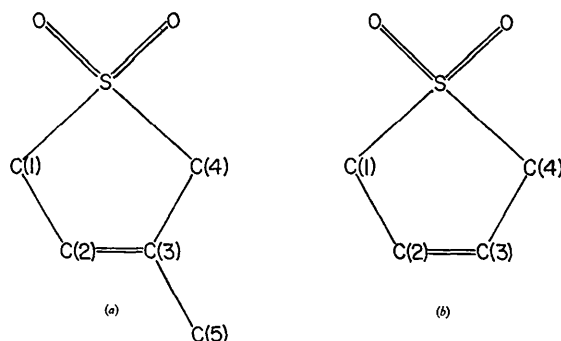


Fig. 1. Atomic numbering used in this paper for (a) β -isoprene sulfone and (b) butadiene sulfone.

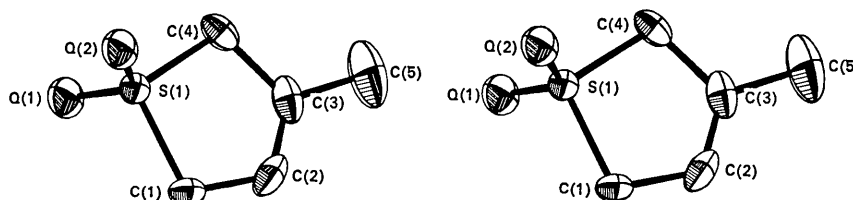


Fig. 2. Stereoscopic representation of the thermal ellipsoids for β -isoprene sulfone.

tors for the hydrogen atoms. The hydrogen atom temperature factors, assigned a value of 6.0, were not refined. The final weighted index was 0.041. The maximum value of the final parameter shifts divided by the estimated standard deviations was 0.14 for the non-hydrogen atoms and 0.20 for the hydrogen atoms. Final atomic parameters are shown in Table 1. Bond lengths and angles were calculated using the *BONDLA* program of X-ray 63 (Stewart, 1964) and are shown in Table 2. The observed and final calculated structure factors are shown in Table 3.

Results

Table 2 summarizes the bond lengths and bond angles of β -isoprene sulfone (this paper) and, for comparison, of butadiene sulfone (Sands & Day, 1967). Equivalent dimensions in the two compounds are quite similar. The C(2)–C(3) bond distance of 1.307 Å is significantly shorter than the value of 1.37 Å reported by Jeffrey (1951) but now agrees well with the equivalent value of 1.299 Å observed in butadiene sulfone. Other distances and angles are in agreement with those observed in a variety of sulfones as discussed by Sands & Day. The ellipsoids of atomic thermal vibration are shown in Fig. 2. As expected, the thermal motion of the

methyl carbon atom is larger than that of the ring carbon atoms.

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References

- BOND, W. (1959). *Acta Cryst.* **12**, 375.
 COX, E. G. & JEFFREY, G. A. (1942). *Trans. Faraday Soc.* **38**, 241.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390.
 EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
 JEFFREY, G. A. (1951). *Acta Cryst.* **4**, 58.
 LADELL, J. (1965). *Norelco Reporter*, **12**, 32.
 SANDS, D. E. & DAY, V. W. (1967). *Z. Kristallogr.* **124**, 220.
 STEWART, J. (1964). *X-Ray 63 Technical Report TR-64-6*, NS 6-398, Computer Science Center, University of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

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The wurtzite z parameter and linear compressibilities for NH_4F^* . By B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.*

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The z parameter in NH_4F has been determined using 108 Mo $K\alpha$ intensity data to be 0.3781 ± 0.0007 . The values of the N–F hydrogen bond separations are 2.707 (5) and 2.709 (5) Å. The linear compressibilities along a and c are 13.6 and $14.6 \times 10^{-13} \text{ cm}^2 \text{ dyne}^{-1}$, respectively.

Introduction

The phase diagram of ammonium fluoride has received much attention and has been summarized by Nabar, Calvert & Whalley (1969). The structure of $\text{NH}_4\text{F(II)}$, obtained at 3.64 kbar pressure (Morosin & Schirber, 1965), has yet to be determined. The two initial objectives of the present pressure studies on $\text{NH}_4\text{F(I)}$ were to determine the compressibilities of the lattice and the pressure change of the wurtzite z parameter prior to the phase transition. An earlier study (Morosin & Schirber, 1969) on the metals Sb and Bi indicated that with proper care and conditions, small differences in structural parameters as a function of pres-

sure could be determined. Unfortunately, this did not prove possible for $\text{NH}_4\text{F(I)}$. The present study reports the linear compressibilities for $\text{NH}_4\text{F(I)}$ below this pressure phase transition as well as the redetermination of the structure for the room-temperature one bar phase.

Structure analysis

$\text{NH}_4\text{F(I)}$ crystallizes with the wurtzite structure in space group $P6_3mc$. In this structure type, the heavy atoms are assigned to special positions on (b) sites at $\frac{1}{3}, \frac{2}{3}, z$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z$ while the hydrogen atoms occupy one such set of sites as well as the sixfold (c) sites at $x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z; \bar{x}, x, \frac{1}{2} + z; \bar{x}, 2\bar{x}, \frac{1}{2} + z$ and $2x, x, \frac{1}{2} + z$. In this polar space group, one of the atoms may be assigned $z = 0.0$. For the remaining heavy atom, Zachariasen (1927) found $z = 0.365$. This result

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