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The Configurations of the Diastereomeric 1-Chloromercuri-2-Methoxycyclohexanes

By A. G. Brook and George F Wright

Department of Chemistry, University of Toronto, Canada

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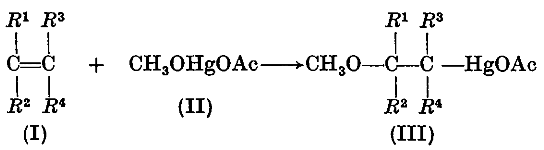
Structure determinations of the α- and β-1-chloromercuri-2-methoxycyclohexanes have shown, contrary to earlier opinions based on chemical evidence, that the α form has the diastereomeric configuration known as *trans* while the β form has the *cis* configuration. The cyclohexane ring in each exists as the puckered or crown form. The structure determination was facilitated by the fact that the chloro-, bromo- and iodomercurials of each diastereoisomer form isostructural crystalline series from which an initial estimate could be made for the relative positions of the halogen and mercury atoms. A new interpretation of the chemical evidence, based on cycloco-ordination, can be obtained from these structure determinations.

Methoxymercuration may be defined as the addition to a carbon–carbon double bond of the elements of methoxy and acetoxymercuri:



$$\underset{(I)}{\begin{matrix} R^1 & R^3 \\ | & | \\ C & = & C \\ | & | \\ R^2 & R^4 \end{matrix}} + \underset{(II)}{CH_3OHgOAc} \longrightarrow \underset{(III)}{CH_3O-\begin{matrix} R^1 & R^3 \\ | & | \\ C & - & C \\ | & | \\ R^2 & R^4 \end{matrix}-HgOAc}$$

The addend (II) evidently originates from a solution of mercuric acetate in methanol. The reaction is of interest as one means of evaluating the detailed mechanism whereby an alkene is converted to an alkane because of certain characteristics. First, the reaction can easily be followed kinetically (Romeyn & Wright, 1947; Connor & Wright, 1946). Secondly, if the alkane (I) is capable of geometric isomerism (either R^1, R^3 or R^2, R^4 are different), then each geoisomer reacts to give a specific uncontaminated diastereoisomer, and the *cis* geoisomer (R^2, R^4 = hydrogen) always reacts more rapidly than the *trans* form (Wright, 1935; Brown & Wright, 1940). Finally, methoxymercuration is accelerated by small amounts of electron acceptors and is inhibited by traces of electron donors (Birks & Wright, 1940). In spite of these favorable diagnostic features, the application of methoxymercuration to studies of reaction mechanism has been limited by the fact that the spatial configuration of the methoxymercurials (III) cannot reliably be dmonstrated by chemical means.

Romeyn & Wright (1947) prepared the two possible diastereoisomers of 1-chloromercuri-2-methoxycyclohexane. Since cyclohexane can exist in but one geoisomeric form, only one of these diastereoisomers (α or *dd, ll*) can be found when the cycloalkene is treated with mercuric acetate in methanol and the product converted by aqueous sodium chloride from the acetoxymercurial to the chloromercurial. The β (*dl, ld*) diastereomer forms the greater part of a mixture produced when the α isomer is subjected to equilibration conditions by introduction of catalysts which produce free radicals. Since the α isomer was less stable and more easily soluble in alkali than the β form, Romeyn & Wright considered that the added groups were closer together in the α than in the β form. This opinion, which specifies that the addition does not occur with a single Walden inversion, will be shown in the present report to be in error.

The positions of the methoxy and mercuri groups in these two diastereomers are fixed relative to the cyclohexane ring, since free rotation cannot occur owing to the cyclic structure. Anionic exchange of acetoxy by chloro, bromo and iodo ions can be accomplished simply and without configurational change to yield well-crystallized compounds. An attempt has been made, therefore, to determine the spatial configurations of these methoxyhalomercurials by X-ray diffraction methods.

The three α (*dd, ll*) halomercurials of methoxycyclohexane were found to exist as an isostructural crystalline series, the unit cell of which was triclinic. In consequence rotation and Weissenberg moving-film photographs had to be taken about each of the three axes. Each unit cell contained two molecules of opposite enantiomeric configuration, consistent with the space group $P\bar{1}$. This isostructural crystalline series is demonstrated in Table 1 by the nearly constant interaxial angles and the regular increase in dimension from chloride to bromide to iodide.

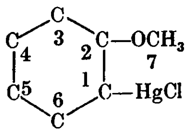
Table 1. *Cell constants for α-(dd, ll)-2-methoxycyclohexylmercuric halides*

	Chloride	Bromide	Iodide
a (A.)	8·20 ± 0·01	8·33 ± 0·02	8·58 ± 0·02
b (A.)	10·58 ± 0·02	10·73 ± 0·03	10·87 ± 0·03
c (A.)	6·07 + 0·01	6·09 ± 0·02	6·12 ± 0·02
α	83° 58′ ± 10′	83° 40′ ± 20′	84° 00′ ± 20′
β	116° 20′ ± 10′	115° 28′ ± 20′	115° 4′ ± 20′
γ	102° 48′ ± 10′	104° 10′ ± 20′	102° 50′ ± 20′
Vol. (A.^{3})	460·2	477·7	504
d (calc.)	2·51	2·74	2·90
d (obs.)	2·50, 2·52	—	—

The stucture determination was carried out on the chloromercurial, and thirty parameters (three for each of the atoms in the molecule exclusive of hydrogen) had to be evaluated. Fourier projections on the principal planes were made using $|F|$ factors derived from the moving-film photographs. The phase determination of the molecular structure factors was simplified by the presence of the heavy mercury atom. The electron-density maps (Figs. 1, 2 and 3) have been idealized by appended schematic diagrams showing atomic positions. Table 2 lists the atomic parameters assumed in calculation of the structure factors.

Table 2. *Atomic parameters for α-(dd, ll)-1-chloromercuri-2-methoxycyclohexane*

Atom	*x*	*y*	*z*
C_1	0·331	0·792	0·946
C_2	0·398	0·764	0·146
C_3	0·458	0·654	0·198
C_4	0·300	0·525	0·075
C_5	0·232	0·549	0·833
C_6	0·158	0·683	0·795
C_7	0·658	0·890	0·500
O	0·533	0·875	0·308
Hg	0·178	0·960	0·864
Cl	0·060	0·146	0·785



From the projections, and three-dimensional scale models constructed from them, it is found that the cyclohexane ring is in the puckered form known as the ‘crown’ or ‘chair’. The projection shows the ring (average C–C bond dimension is 1·56 ± 0·1 A., while average cyclic bond angle is 113 ± 10°) to be somewhat distorted, but this may not be real. The presence of the heavy atoms mercury and chlorine (total 97 electrons) causes large experimental error in position of the carbon atoms, which have relatively weak scattering power (6 electrons).

The C–Hg–Cl bond angle was determined as 178°, with C–Hg and Hg–Cl bond dimensions of 2·34 and 2·53 A. respectively. The positions of the methoxy and

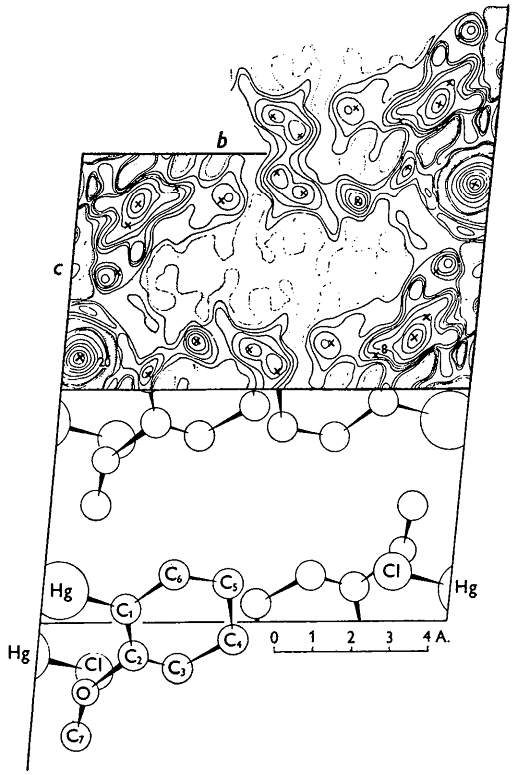


Fig. 1. *trans*-1-Chloromercuri-2-methoxycyclohexane; *a*-axis projection.

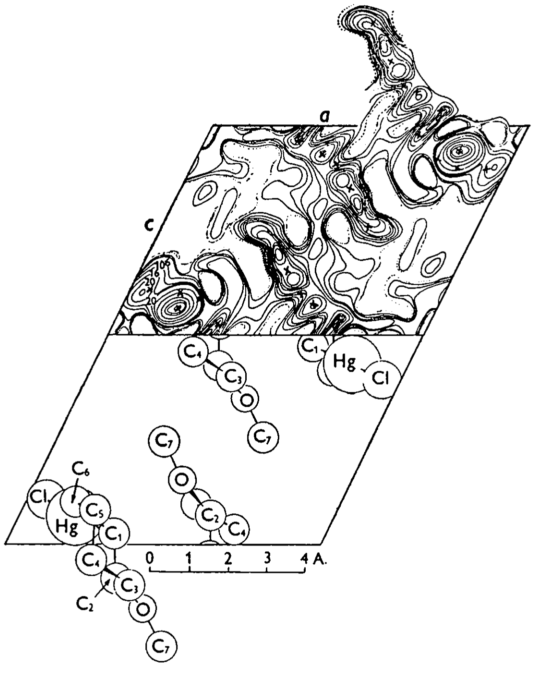


Fig. 2. *trans*-1-Chloromercuri-2-methoxycyclohexane; *b*-axis projection.

chloromercuri relative to the ring involve a Hg–O dimension of 4·06 A. If one were to imagine the ring as planar (with 120° angles), then this Hg–O dimension would magnify to the diastereomeric configuration known as '*trans*', wherein the methoxy and chloromercuri groups would be on opposite sides of this plane.

The structure of the product from cyclohexene methoxymercuration was confirmed by a similar study of the *β* (*dl*, *ld*) diastereomer. None of this isomer is produced by methoxymercuration, but it can be separated as the more stable form in the equilibrium mixture and *α* and *β* diastereomers which is formed when *α*-2-methoxycyclohexylmercuric chloride is isomerized with a free-radical source such as benzoyl peroxide (Romeyn & Wright, 1947). This diastereomeric chloromercurial can be converted by anion interchange to the bromomercurial. Either the chloromercurial or the bromomercurial can be converted to the iodomercurial by treatment with aqueous sodium iodide solution in the same manner. These three *β*-halomercurials, like the *α* series, also form an isostructural crystalline series with two enantiomeric molecules related in a triclinic cell by a center of inversion (space group $P\bar{1}$). The similarity of interaxial angle and expected gradations in cell dimension are shown in Table 3.

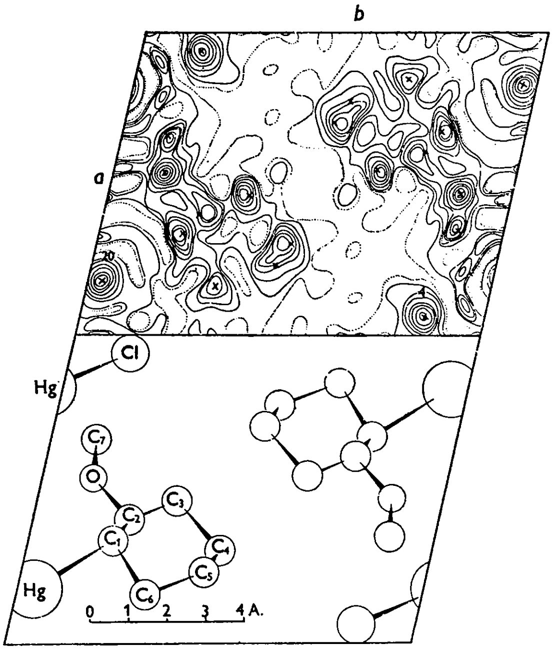


Fig. 3. *trans*-1-Chloromercuri-2-methoxycyclohexane; c-axis projection.

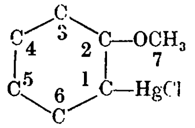
The chloromercurial was selected fron this series for structure determination so as to establish comparison with the *α* configuration. The atomic parameters are tabulated in Table 4. The electron-density maps together with schematic diagrams are shown in Figs. 4, 5 and 6. They show that in this series the ring is again in the puckered or crown form. Refinement in the Fourier analysis has decreased the distortion, so that the average C–C bond distance is 1·52 ± 0·07 A. and the average cyclic bond angle is 109° ± 7° (as compared with 1·54 A. and 109° 28′ for normal bonds in cyclohexane (Hassel & Ottar, 1942)).

Table 3. *Cell constants for β-(dl, ld)-2-methoxycyclohexylmercuric halides*

	Chloride	Bromide	Iodide
a (A.)	7·88 ± 0·01	7·96 ± 0·02	8·18 ± 0·02
b (A.)	9·29 ± 0·01	9·41 ± 0·02	9·63 ± 0·02
c (A.)	6·37 ± 0·01	6·46 ± 0·02	6·57 ± 0·02
α	88° 29′ ± 10′	86° 22′ ± 20′	84° 36′ ± 20′
β	102° 18′ ± 10′	102° 00′ ± 20′	102° 52′ ± 20′
γ	92° 57′ ± 10′	93° 40′ ± 20′	94° 49′ ± 20′
Vol. (A.^{3})	455·1	471·6	503
d (calc.)	2·55	2·77	2·91
d (obs.)	2·54	—	—

Table 4. *Atomic parameters of β-(dl, ld)-1-chloromercuri-2-methoxycyclohexane*

Atom	*x*	*y*	*z*
C_1	0·358	0·769	0·969
C_2	0·483	0·757	0·790
C_3	0·385	0·675	0·600
C_4	0·286	0·547	0·660
C_5	0·151	0·584	0·794
C_6	0·253	0·650	0·004
C_7	0·700	0·862	0·643
O	0·578	0·867	0·764
Hg	0·221	0·951	0·879
Cl	0·069	0·154	0·788



The C–Hg–Cl bond angle was found to be the expected 180° with an internuclear distance of 2·50 A. for Hg–Cl and an internuclear distance of 2·15 A. for C–Hg. From these dimensions in the scale model the O–Hg dimension is 3·06 A. If the scale model is altered to bring the ring into planarity (120° bond angles) then the methoxy and chloromercuri groups are in the diastereomeric relationship known as *cis*, i.e. both on the same side of the plane.

As a criterion for the accuracy of the structure determination, the mean discrepancy expressed as

$$\frac{\Sigma(|F_{\text{obs.}}| - |F_{\text{calc.}}|)}{\Sigma |F_{\text{obs.}}|}$$

has been evaluated as a percentage for each projection, including those factors for which $F_{\text{obs.}}$ is zero. The values are:

Isomer	*hk*0	0*kl*	*h*0*l*	Overall
α	8·9	10·3	10·5	9·9
β	10·6	13·3	16·4	13·4

These low values must be attributed to the powerful contribution of the heavy mercury atom to the various structure factors.

In view of these unequivocal results it is evident that the former designation (Romeyn & Wright, 1947) of

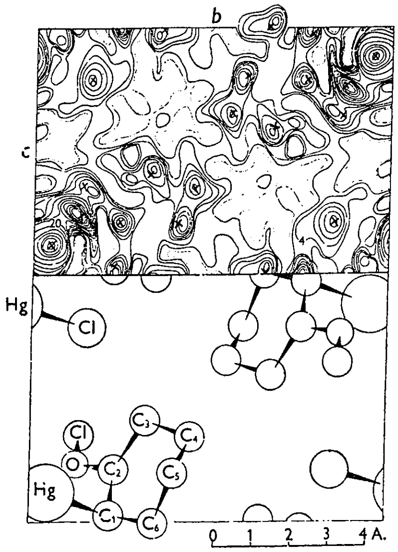


Fig. 4. *cis*-1-Chloromercuri-2-methoxycyclohexane; *a*-axis projection.

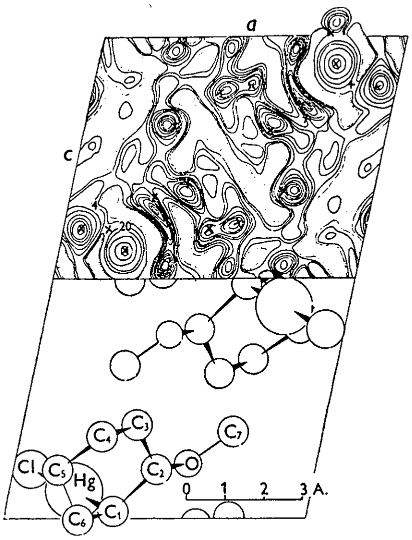
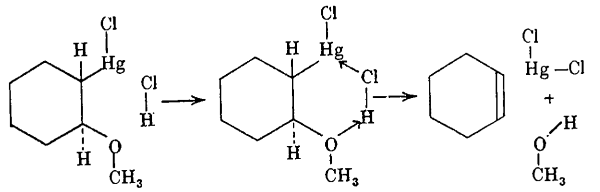
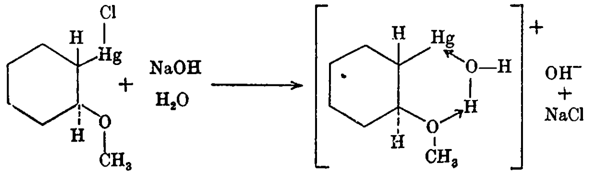


Fig. 5. *cis*-1-Chloromercuri-2-methoxycyclohexane; *b*-axis projection.

the diastereomeric *cis* configuration for α-1-chloromercuri-2-methoxycyclohexane is no longer tenable. It must be concluded that the interpretation of the chemical evidence (that the diastereomer in which the mercury and methoxyl oxygen are closer is least stable and most soluble in alkali) is erroneous. An alternative explanation for these phenomena, based on the present stereochemical information, may be derived from a consideration of the '*c*' projection of the *trans* diastereoisomer shown in Fig. 3. If the hydrogen chloride, which is effective as a hydrolyzing agent for the mercurial, co-ordinates with it to form a second ring, this may decompose to cyclohexene, mercuric chloride and methanol. It may be seen from Fig. 3 that the probability of such fused ring formation would be high because both rings would be in the strainless 'chair' or crown form. Reference to the '*c*' projection of the *cis*-diastereomer in Fig .6 shows that cyclo-co-ordination



would involve the much less probable bicyclic intermediate wherein one ring would be in the 'chair' and one in the 'boat' form. Thus if cyclo-co-ordination were a prelude to hydrolysis the *trans* (α) diastereomer might be expected to hydrolyze more easily (as in fact it does) than the *cis* (β) isomer. A similar argument suffices to explain the greater solubility of the α-1-chloromercuri-2-methoxycyclohexane in alkali.



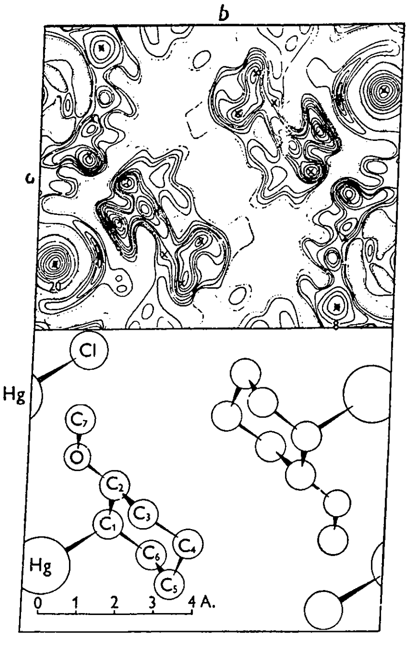


Fig. 6. *cis*-1-Chloromercuri-2-methoxycyclohexane; *c*-axis projection.

Experimental

Single-crystal preparation of halomercurials

Crystals of all the halomercurials investigated (Wright, 1935; Romeyn & Wright, 1947; Brook & Wright, 1950) were formed by slow evaporation of chloroform solutions (or benzene solutions of chloromercurials) as thin platelets tabular on (010) with (100) and (001) usually the only other forms present. Thin needles about $0{\cdot}2\times0{\cdot}2$ mm. in cross-section were cut from the edges of the plates for rotation about the a or c axes. For rotation about the b axis small triangles of edge length 0·3–0·5 mm. were obtained by chopping off the acute angle from a plate of suitable thickness.

Reflexions and intensities

Rotation and Weissenberg exposures were made about each of the three crystal axes using copper $K\alpha_1$ radiation ($\lambda = 1{\cdot}5405$ A.). All possible reflexions up to $2\sin\theta = 1{\cdot}95$ were used, totalling over 400 for each compound. Relative intensities of these reflexions were estimated visually from a series of accurately timed exposures by comparison with a density wedge made with the same crystal which was used for the Weissenberg exposures. This wedge was a composite photograph of a single reflexion recorded for different exposure times by using each 5° oscillation about the position of reflexion as a unit of intensity. About 40 differences of relative intensity ranging from 1 to 50 or 60 could be made on a single film by moving the camera about 3 mm. between each series of oscillations. (We are grateful to Prof. Cox of Leeds University for personal advice on the use of this method.) Comparison of the Weissenberg exposures with this wedge furnished a relative-intensity range of about 2000 to 1.

Structure determination

The presence of the heavy mercury atom greatly simplified the determination of the phases of each reflexion since in most cases the mercury-scattering contribution to the molecular structure factor completely dominated the contributions of all the other atoms. By calculation of trial structures an approximate position for the mercury atom was found. The phases of its contributions to the stronger reflections could then be derived. These phases, together with the molecular structure factors derived from the estimated intensities, were used in preliminary Fourier summations using photographic masks (Huggins, 1941) kindly donated by Dr Huggins. These rapid summations gave quite accurately the positions of the mercury and chlorine atoms from which a decision could be made regarding phases of all observed reflexions. Complete summations using all reflexions were then carried out using Patterson–Tunell strips. Each summation was evaluated at 1800 points in the asymmetric unit (half unit cell). Most of the atoms were resolved in the projections, though numerous spurious peaks were encountered. Scale models helped in decisions whether peaks were real or spurious. A complete set of structure factors was calculated from this approximate structure. Phase corrections were made where necessary. Observed and calculated intensities were generally in satisfactory agreement at reflexion angles less than $\sin\theta = 0{\cdot}7$, but the observed values tended to be low at higher angles. Since the latter spots were indefinite and diffuse, another complete set of Weissenberg photographs were taken using smaller crystals than those first employed. After a complete re-estimation of intensities was made, the final Fourier summations were completed as illustrated in Figs. 1–6. The contours, drawn in the region of the atomic positions by graphical interpolation (using sections along both axial directions) are at intervals of 1 e.A.$^{-2}$ (the 1-electron line being dotted) except in the region of the heavy atoms. The contours for the mercury atoms are drawn at intervals of 20 e.A.$^{-2}$, and those for the chlorine atoms at intervals of 4 e.A.$^{-2}$, starting at the numbered contour lines. The number of terms used in each of the three projections (ab, bc and ac) were, respectively, 193, 144 and 107 (total, 415) for the α-(dd, ll)-1-chloromercuri-2-methoxycyclohexane; for the β-(dl, ld) diastereomer 182, 147 and 125 (total, 427) terms were used. Table 5 lists the $F_{\text{calc.}}$ and F_{obs} values for each of the planes (hkl) observed.

The average value of each parameter obtained from the contour maps and expressed as decimal fractions of an axial length of unity for every atom, was used for the evaluation of the $F_{\text{calc.}}$ values recorded in Table 5. The crosses on the contour maps indicate the final positions of the atoms. The final electron-density maps show few spurious peaks of significant height except for the annular ring about the mercury atom.

Calculation of the molecular structure factors was carried out in the usual manner, employing values of atomic scattering factors recorded in the literature (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1944, p. 571). Comparison of the experimental and calculated F values indicated that a large temperature correction factor was required. Since the accuracy of our work did not justify calculation of experimental atomic scattering factors, an artificial factor was employed. The ratio $F_{\text{obs.}}/F_{\text{calc.}}$ was plotted against $\sin\theta/\lambda$ for every reflection in the zone under consideration and a smooth curve was drawn among the points. The values of $F_{\text{obs.}}$ were then multiplied by the factor required to make $F_{\text{obs.}}/F_{\text{calc.}}$ equal to unity at $\sin\theta/\lambda = 0$. The remaining $F_{\text{obs.}}/F_{\text{calc.}}$ values were then adjusted appropriately.

This re-evaluated curve had the approximate form $\exp[-B(\sin\theta/\lambda)^2]$, where the temperature correction factor B approximates 3×10^{-16} cm.^{2} Appropriate correction factors were then found for each reflexion and applied in the usual manner (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, 1944, pp. 569–70).

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Table 5. *Observed and calculated values of the structure factors*

	β compound		α compound	
hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$
000	—	324	—	324
010	145	151	160	163
020	91	91	100	110
030	51	47	51	57
040	22	13	42	38
050	8	4	24	22
060	13	−12	26	20
070	26	−24	<12	−6
080	46	−40	24	−22
090	48	−42	30	−26
0,10,0	49	−46	47	−46
0,11,0	34	−32	43	−43
0,12,0	—	—	29	−28
0,13,0	—	—	17	−18
100	18	17	56	55
110	87	82	100	110
$1\bar{1}0$	33	−23	19	18·5
120	68	69	75	85
$1\bar{2}0$	9	−4	26	25
130	98	103	88	97
$1\bar{3}0$	110	−98	34	−35
140	100	107	89	100
$1\bar{4}0$	113	−118	54	−65
150	126	121	115	113
$1\bar{5}0$	113	−109	89	−89
160	101	96	100	95
$1\bar{6}0$	88	−86	67	−74
170	62	62	80	81
$1\bar{7}0$	58	−61	68	−74
180	20	9	31	27·5
$1\bar{8}0$	50	−39	60	−61
190	0	−4	17	13
$1\bar{9}0$	39	−31	63	−65
1,10,0	0	−4	0	3
$1,\overline{10},0$	16	−14	49	−51
1,11,0	13	−11	0	−4·6
$1,\overline{11},0$	0	3	35	−33
1,12,0	—	—	<12	−7·5
$1,\overline{12},0$	—	—	20	−15
$1,\overline{13},0$	—	—	10	−5
200	120	−122	68	−70
210	102	−102	44	−42
$2\bar{1}0$	95	−94	65	−75
220	96	−92	47	−40
$2\bar{2}0$	136	−137	119	−123
230	34	−38	18	10
$2\bar{3}0$	143	−135	135	−130
240	0	1	21	24
$2\bar{4}0$	87	−80	171	−155
250	22	36	36	50
$2\bar{5}0$	48	−44	110	−106
260	45	53	59	64
$2\bar{6}0$	11	−2	56	−62
270	58	53	65	66
$2\bar{7}0$	30	30	40	−38
280	55	59	54	62
$2\bar{8}0$	34	32	24	−18
290	44	36	41	38
$2\bar{9}0$	37	33	10	−8
2,10,0	36	33	35	33
$2,\overline{10},0$	31	30	7	−6
2,11,0	25	24	26	25
$2,\overline{11},0$	24	22	0	2
2,12,0	—	—	17	19·5
$2,\overline{12},0$	—	—	19	11
$2,\overline{13},0$	—	—	18	15
300	57	−57	109	−107
310	102	−107	121	−119
$3\bar{1}0$	17	−8	86	−84
320	125	−131	129	−119
$3\bar{2}0$	22	26	69	−64
330	131	−127	103	−103
$3\bar{3}0$	55	49	65	−60
340	88	−86	37	−46
$3\bar{4}0$	43	54	47	−44
350	62	−60	28	−27
$3\bar{5}0$	53	54	21	−16
360	35	−32	12	−6
$3\bar{6}0$	73	73	<11	−7·5
370	31	−31	7	−5
$3\bar{7}0$	70	70	33	30
380	17	−14	<17	8
$3\bar{8}0$	57	55	47	54
390	0	1	7	12
$3\bar{9}0$	53	43	48	51
3,10,0	19	15	25	21
$3,\overline{10},0$	22	14	42	45
3,11,0	23	22	19	20
$3,\overline{11},0$	9	4	32	36
$3,\overline{12},0$	—	—	27	24
$3,\overline{13},0$	—	—	22	19
400	84	79	21	−21
410	41	41	49	−59
$4\bar{1}0$	106	109	14	14
420	24	14	54	−58
$4\bar{2}0$	106	115	40	36
430	0	−8	64	−76
$4\bar{3}0$	99	97	50	46
440	17	−24	60	−72
$4\bar{4}0$	65	71	54	58
450	37	−36	45	−52
$4\bar{5}0$	45	39	50	51
460	50	−50	44	−48
$4\bar{6}0$	30	27	66	66
470	51	−55	42	−43
$4\bar{7}0$	2	9	66	75
480	47	−50	32	−39
$4\bar{8}0$	0	5	65	62
490	38	−35	24	−26
$4\bar{9}0$	24	−14	55	52
4,10,0	21	−24	13	−14
$4,\overline{10},0$	25	−25	30	34
$4,\overline{11},0$	35	−24	20	14
$4,\overline{12},0$	—	—	<10	6
500	66	59	56	57
510	65	64	35	30
$5\bar{1}0$	69	62	73	78
520	65	63	<17	11
$5\bar{2}0$	44	43	85	91
530	77	81	18	17
$5\bar{3}0$	9	16	78	88
540	66	70	0	0·2
$5\bar{4}0$	26	−26	65	68
550	49	45	<17	−9
$5\bar{5}0$	44	−48	45	47
560	32	23	31	−26
$5\bar{6}0$	45	−52	30	30

Table 5 (*cont.*)

	β compound		α compound	
hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$F_{\text{calc.}}$
570	0	− 2	32	−34
$5\bar{7}0$	42	−51	33	26
580	16	−18	35	−39
$5\bar{8}0$	40	−35	20	18
590	27	−14	27	−25
$5\bar{9}0$	28	−28	< 17	9
5,10,0	23	−16	—	—
$5,\overline{10},0$	34	−16	< 13	− 7
$5,\overline{11},0$	—	—	25	−15
$5,\overline{12},0$	—	—	22	−21
600	40	−42	56	58
610	23	−17	47	52
$6\bar{1}0$	54	−56	52	55
620	< 13	12·5	56	56
$6\bar{2}0$	56	−60	51	45
630	26	30	51	49
$6\bar{3}0$	55	−54	32	30
640	40	55	42	43
$6\bar{4}0$	51	−53	< 14	9
650	42	43	33	31
$6\bar{5}0$	49	−41	< 17	−10
660	36	31	21	18
$6\bar{6}0$	39	−46	30	−24
670	31	30	0	2
$6\bar{7}0$	25	−22	33	−30
680	26	26	0	− 2
$6\bar{8}0$	0	− 4	33	−32
690	24	20	—	—
$6\bar{9}0$	14	5	30	−27
$6,\overline{10},0$	—	—	27	−26
$6,\overline{11},0$	—	—	24	−25
700	51	−57	< 14	− 6
710	59	−64	< 14	3
$7\bar{1}0$	45	−46	< 14	−16
720	40	−40	15	16
$7\bar{2}0$	20	−23	20	−15
730	37	−40	30	35
$7\bar{3}0$	12	−25	24	−20
740	33	−28	36	43
$7\bar{4}0$	0	− 1	39	−36
750	0	− 8	32	36
$7\bar{5}0$	0	3	42	−43
760	0	− 3	31	31
$7\bar{6}0$	< 12	14	45	−47
770	10	6	26	20
$7\bar{7}0$	21	27	47	−40
780	12	4	< 14	11
$7\bar{8}0$	37	25	34	−30
$7\bar{9}0$	—	—	25	−20
$7,\overline{10},0$	—	—	< 11	− 8
800	10	− 1	34	−40
810	< 13	−14	25	−23
$8\bar{1}0$	10	9	37	−38
820	22	−21	19	−13
$8\bar{2}0$	25	28	40	−37
830	23	−12	< 12	− 6
$8\bar{3}0$	34	39	31	−31
840	32	−26	0	1·7
$8\bar{4}0$	48	43	29	−29
850	23	−31	0	2·2
$8\bar{5}0$	41	36	27	−22
860	29	−33	—	—
$8\bar{6}0$	25	26	23	−21
$8\bar{7}0$	20	11	< 13	− 8
$8\bar{8}0$	—	—	0	− 0·5
900	23	25	15	−18
910	25	37	17	−21
$9\bar{1}0$	20	24	17	−15
920	16	27	—	---
$9\bar{2}0$	25	24	< 11	− 7
930	8	17	—	—
$9\bar{3}0$	21	21	< 10	− 0·5
940	0	6	—	—
$9\bar{4}0$	< 15	15	—	—
001	105	121	107	114
011	50	61	73	72
$0\bar{1}1$	146	145	70	67
021	34	30	61	60
$0\bar{2}1$	107	105	88	85
031	20	−20	< 8	1·8
$0\bar{3}1$	131	120	100	105
041	51	−44	27	−24
$0\bar{4}1$	111	94	122	128
051	70	−67	60	−64
$0\bar{5}1$	91	83	113	118
061	67	−62	63	−64
$0\bar{6}1$	32	29	83	81
071	63	−55	69	−72
$0\bar{7}1$	0	0·7	55	46
081	46	−39	57	−59
$0\bar{8}1$	8	− 9	24	15
091	44	−34	45	−42
$0\bar{9}1$	24	−18	0	− 3
0,10,1	36	−29	47	−52
$0,\overline{10},1$	22	−16	0	− 9
0,11,1	21	−15	34	−34
$0,\overline{11},1$	23	−18	13	−11
0,12,1	—	—	22	−23
$0,\overline{12},1$	—	—	14	−10
0,13,1	—	—	11	−10
$0,\overline{13},1$	—	—	12	−10
002	25	−26	59	−41
012	33	−33	42	−50
$0\bar{1}2$	< 10	14	0	6
022	57	−57	51	−57
$0\bar{2}2$	57	67	37	50
032	44	−45	75	−79
$0\bar{3}2$	102	106	68	68
042	77	−73	77	−75
$0\bar{4}2$	107	105	88	90
052	85	−91	82	−86
$0\bar{5}2$	88	90	84	79
062	76	−71	77	−83
$0\bar{6}2$	65	65	64	59
072	65	−65	63	−68
$0\bar{7}2$	30	26	55	53
082	40	−31	45	−45
$0\bar{8}2$	28	22	47	52
092	8	− 7	29	−28
$0\bar{9}2$	14	12	38	37
0,10,2	0	1	17	−13
$0,\overline{10},2$	0	4	38	38
0,11,2	0	4	0	− 5
$0,\overline{11},2$	0	− 2	23	20
0,12,2	—	—	0	− 3
$0,\overline{12},2$	—	—	10	7
003	65	−77	123	−106
013	84	−98	103	−93
$0\bar{1}3$	33	−42	46	−52
023	81	−97	101	−96
$0\bar{2}3$	0	1	25	−26
033	67	−77	77	−77
$0\bar{3}3$	18	24	12	−18
043	65	−64	62	−59
$0\bar{4}3$	32	40	0	3
053	53	−49	46	−47
$0\bar{5}3$	37	39	12	8
063	35	−31	37	−44
$0\bar{6}3$	45	48	20	28
073	30	−25	19	−24
$0\bar{7}3$	43	46	28	36

Table 5 (*cont.*)

	β compound		α compound	
hkl	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$
083	0	−3	9	−9
$0\bar{8}3$	41	38	40	46
093	20	14	< 13	−2
$0\bar{9}3$	32	32	41	37
0,10,3	21	15	12	13
$0,\overline{10},3$	16	15	41	37
0,11,3	20	17	13	19
$0,\overline{11},3$	12	7	29	22
0,12,3	—	—	14	17
$0,\overline{12},3$	—	—	< 8	16
004	65	−72	71	−69
014	57	−73	60	−65
$0\bar{1}4$	54	−62	58	−57
024	70	−85	58	−58
$0\bar{2}4$	42	−50	61	−54
034	47	−55	25	−31
$0\bar{3}4$	39	−42	61	−60
044	19	−22	18	−20
$0\bar{4}4$	25	−27	59	−55
054	0	0·2	6	3
$0\bar{5}4$	0	2·3	39	−41
064	< 14	13	< 14	12
$0\bar{6}4$	7	13	16	−8
074	17	16	18	26
$0\bar{7}4$	28	29	0	−2
084	26	22	21	23
$0\bar{8}4$	27	32	14	10
094	25	18	22	21
$0\bar{9}4$	24	25	18	12
0,10,4	20	19	22	17
$0,\overline{10},4$	15	15	17	13
005	26	−27	20	−12
015	28	−27	11	−8
$0\bar{1}5$	41	−51	29	−31
025	24	−22	0	−0·7
$0\bar{2}5$	47	−60	34	−42
035	0	−1·7	17	16
$0\bar{3}5$	44	−58	40	−48
045	10	6·5	21	14
$0\bar{4}5$	32	−42	44	−47
055	21	21	26	26
$0\bar{5}5$	14	−16	36	−38
065	22	29	29	32
$0\bar{6}5$	10	−7	26	−22
075	31	35	27	36
$0\bar{7}5$	0	−2	22	−22
085	28	27	20	25
$0\bar{8}5$	0	6	17	−16
095	21	19	16	20
$0\bar{9}5$	7	7	13	−10
006	< 14	−8	16	17
016	< 14	7	21	25
$0\bar{1}6$	22	−22	0	0·8
026	17	27	25	30
$0\bar{2}6$	20	−35	11	−7
036	23	31	23	31
$0\bar{3}6$	27	−39	10	−12
046	24	36	22	24
$0\bar{4}6$	24	−29	13	−13
056	23	23	18	19
$0\bar{5}6$	17	−21	18	−15
066	21	24	17	16
$0\bar{6}6$	22	−24	19	−17
076	19	22	—	—
$0\bar{7}6$	21	−18	—	—
086	17	15	—	—
007	6	7	24	17
017	15	20	—	—
$0\bar{1}7$	< 12	5	—	—
027	17	27	—	—
$0\bar{2}7$	< 12	10	—	—
037	26	32	—	—
$0\bar{3}7$	< 11	−27	—	—
047	22	27	—	—
$0\bar{4}7$	12	−12	—	—
057	19	13	—	—
$0\bar{5}7$	10	−13	—	—
101	130	137	170	170
$\bar{1}01$	90	−92	80	−74
201	20	−28	38	38
$\bar{2}01$	135	−148	160	−179
301	90	−97	64	−68
$\bar{3}01$	0	5	80	−66
401	26	26	74	−67
$\bar{4}01$	82	89	44	45
501	99	90	14	10
$\bar{5}01$	12	10	69	80
601	35	26	69	60
$\bar{6}01$	111	−88	< 12	8
701	63	−59	43	43
$\bar{7}01$	52	−39	57	−51
801	32	−29	14	−13
$\bar{8}01$	52	44	44	−49
901	27	25	—	—
$\bar{9}01$	46	36	< 15	−5·4
$\overline{10},0,1$	13	−13	—	—
102	103	117	83	82
$\bar{1}02$	130	−140	160	−146
202	21	25	75	84
$\bar{2}02$	100	−91	120	−129
302	101	−74	< 11	−4
$\bar{3}02$	98	97	55	61
402	57	−51	71	−65
$\bar{4}02$	65	63	100	89
502	64	62	41	−49
$\bar{5}02$	52	−42	49	49
602	65	62	24	28
$\bar{6}02$	76	−65	41	−41
702	< 12	−11	40	38
$\bar{7}02$	20	14	52	−61
802	35	−36	—	—
$\bar{8}02$	72	70	< 19	−9
902	0	1	—	—
$\bar{9}02$	7	12	28	22
$\overline{10},0,2$	20	−30	29	29
103	48	49	< 10	−10
$\bar{1}03$	117	−106	100	−98
203	49	48	71	76
$\bar{2}03$	39	38	15	25
303	18	−13	35	36
$\bar{3}03$	113	115	98	102
403	83	−86	25	−26
$\bar{4}03$	21	22	75	91
503	15	−8	53	−55
$\bar{5}03$	70	−74	26	−28
603	45	60	19	−21
$\bar{6}03$	35	−24	59	−59
703	< 20	22	—	—
$\bar{7}03$	72	62	31	−32
803	19	−26	—	—
$\bar{8}03$	52	40	38	38
$\bar{9}03$	36	−25	49	40
$\overline{10},0,3$	28	−32	—	—
104	< 11	−12	54	−46
$\bar{1}04$	18	−15	15	6
204	72	80	20	16
$\bar{2}04$	106	111	80	94
304	20	19	51	57
$\bar{3}04$	55	58	80	88
404	41	−58	18	13

Table 5 (*cont.*)

	β compound		α compound	
hkl	$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$
$\bar{4}04$	51	−49	<17	3
504	36	−47	21	−23
$\bar{5}04$	55	−57	61	−64
604	21	19	—	—
$\bar{6}04$	23	22	51	−51
704	22	30	—	—
$\bar{7}04$	60	49	22	14
$\bar{8}04$	<20	− 4	59	46
$\bar{9}04$	47	−38	18	19
105	35	−50	48	−49
$\bar{1}05$	27	41	57	50
205	33	46	19	−11
$\bar{2}05$	60	46	82	79
305	36	59	27	23
$\bar{3}05$	<14	−13	14	2
405	<10	− 6	29	31
$\bar{4}05$	69	−84	46	−53
505	34	−50	—	—
$\bar{5}05$	20	−16	54	−61
605	10	− 7	—	—
$\bar{6}05$	45	43	<19	−17
$\bar{7}05$	15	18	25	38
$\bar{8}05$	27	−29	21	19
$\bar{9}05$	29	−33	—	—
106	33	−50	20	−23
$\bar{1}06$	36	55	46	44
206	<13	−10	28	−25
$\bar{2}06$	20	15	24	14
306	29	55	—	—
$\bar{3}06$	48	−58	46	−43
406	18	28	—	—
$\bar{4}06$	36	−48	54	−59
506	13	−29	—	—
$\bar{5}06$	19	21	<12	−14
$\bar{6}06$	36	40	27	26
$\bar{7}06$	<11	− 5	22	35
$\bar{8}06$	22	−31	—	—
107	10	−33	—	—
$\bar{1}07$	24	37	21	19
207	14	−35	—	—
$\bar{2}07$	<12	−15	23	−20
307	<8	16	—	—
$\bar{3}07$	27	−48	47	−38
407	<15	32	—	—
$\bar{4}07$	<12	− 7	22	−19
$\bar{5}07$	30	47	22	27
$\bar{6}07$	19	22	37	31
$\bar{7}07$	15	27	—	—

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A Refinement of the Crystal Structure Analysis of β-Isoprene Sulphone

By G. A. Jeffrey

The Department of Inorganic and Physical Chemistry, The University of Leeds, England

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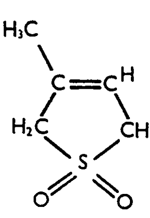
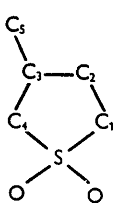
The results of the crystal structure analysis of β-isoprene sulphone published in 1942 have been corrected for the termination-of-series errors. These corrections are considerable, producing changes in the atomic co-ordinates up to 0·06 A. and comparable amendment of the interatomic distances. The new C–C bond lengths are 1·47 A. for the two formal single bonds and 1·38 A. for the double bond. The mean C–S bond length is 1·74 A., and the S–O bond length is 1·44 A. A calculation of the standard deviation of these values indicates that with the exception of the S–O and C–C double bond lengths they are significantly different from the bond lengths associated with the normal representation of the molecule. There is some evidence to show that methylene groups are often 'activated' by adjacent sulphone groups, and the shortening of the formal single bonds may be a general feature of such molecules; but further experimental evidence is necessary.

Introduction

The crystal structure analysis of β-isoprene sulphone by Cox & Jeffrey (1942) revealed a heterocyclic ring compound in which the characters of the bonds were not adequately described by the usual representation (I). Instead of interatomic distances corresponding closely to integral bond orders, the values which they deduced from the Fourier synthesis of the X-ray data were

$$C_1\text{–}C_2 = C_3\text{–}C_4 = 1{\cdot}41,\ C_2\text{–}C_3 = 1{\cdot}42,\ C_3\text{–}C_5 = 1{\cdot}54\ \text{A.},$$
$$C_1\text{–}S = 1{\cdot}74,\quad C_4\text{–}S = 1{\cdot}75\ \text{A.},$$
$$S\text{–}O = 1{\cdot}44\ \text{A.}$$





(I)

Only the lengths of the bonds external to the ring agreed within the estimated experimental error with the standard values of 1·545 A. for a carbon single bond, 1·34 A. for a carbon double bond, and 1·43 A. for a S–O double bond. The C–C bonds in the ring showed the largest discrepancies, which amounted to a decrease of 0·13 A. in the length of the bonds represented as single, and an increase of 0·08 A. in the formal double bond. The