

The Crystal Structure of Braggite, (Pt,Pd,Ni)S*

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(Received 22 December 1972; accepted 7 March 1973)

The determination of the crystal structure of braggite by Patterson methods confirms the proposal of Gaskell [*Z. Kristallogr.* (1935) **96**, 203–213], that braggite is isostructural with PdS. The cell dimensions are $a = 6.380(1)$, $c = 6.570(1)$ Å, $Z = 8$ and the space group is $P4_2/m$. Full-matrix least-squares procedures were used with two sets of merged 4-circle diffractometer data to refine the atomic parameters to an R value of 0.068. Generalized absorption corrections were applied. Several different configurations of metal ordering were tested for the stoichiometric composition $Pt_5Pd_2NiS_8$. It is proposed that the two Pd atoms preferentially occupy the site $2(d), (0, \frac{1}{2}, \frac{1}{2})$, in the structure and that this is the minimum requirement in the formation of the PdS (braggite or vysotskite) structure rather than the PtS (cooperite) structure.

Introduction

Braggite (Pt,Pd,Ni)S is found with significantly varying metal ratios (all with Pt, Ni > Pd) in the ore deposits of the Rustenburg and Potgietersrust districts, Transvaal, South Africa (Cabri, 1972). It was first reported by Bannister (1932) as being isomorphous with the structure of palladium sulphide and was named in honour of Sir William Henry Bragg and Professor William Lawrence Bragg as being the first new mineral to be discovered by X-ray methods alone. The structure of PdS was studied by Gaskell (1935) using single-crystal photographic methods and the structure of braggite was inferred from this study.

The mineral vysotskite (Pt,Pd,Ni)S which has a composition close to PdS (Pd > Pt, Ni) has been reported by Genkin & Zvyagintsev (1962) to be isostructural with PdS and braggite. The PdS structure has distorted Pd tetrahedral coordination about the sulphur atoms, and three different distorted square-planar environments about the palladium. The purpose of the present investigation was to determine the ordering of the Pt and Pd atoms in the braggite structure and thus provide a suitable comparison with the structures of PdS and PtS, and a better understanding of the PdS → vysotskite → braggite → cooperite relationships in the Pd–Pt–S system.

Experimental

Crystal data

Source: Potgietersrust district, Transvaal, South Africa. Chemical composition based on microprobe analysis (Cabri, 1972): $(Pt_{0.64}Pd_{0.27}Ni_{0.14})S_{1.00}$

* Mineral Research Program – Sulphide Research Contribution No. 55.

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Space group: $P4_2/m$

Cell dimensions: $a = 6.380(1)$, $c = 6.570(1)$ Å,
 $Z = 8$, $D_{calc} = 9.34$ g cm⁻³, $D_{meas} \sim 10$ g cm⁻³

(Bannister, 1932)

Cell content based on $Z = 8$: $Pt_5Pd_2NiS_8$

Linear absorption coefficient: $\mu(Mo K\alpha) = 748$ cm⁻¹

Intensity data: 2297 reflexions measured twice.

Several crystals from the Potgietersrust district, Transvaal, South Africa, were obtained from Dr L. J. Cabri of the Mineral Sciences Division, Mines Branch. A small well-defined prism with a maximum dimension of 0.082 mm was selected for data collection. Because of the large absorption coefficient, attempts were made to grind a small crystal sphere but these were unsuccessful, both because of the limited material available and because of the tendency to fracture during the grinding process. Generalized absorption corrections, based on the regular crystal faces, proved to be sufficient for the structure analysis. Precession photographs showed diffraction patterns that are consistent with the previously reported space-group symmetries $P4_2$ or $P4_2/m$. Later analysis of both the Friedel-related intensities and the application of anomalous-scattering corrections in the refinement process determined the correct space group as $P4_2/m$. The crystal was mounted in a random orientation on a 4-circle Picker diffractometer and automatically aligned using 24 independent reflexions, at room temperature (20 °C). A least-squares fit of the measured angles 2θ , ϕ , χ and ω of these reflexions, assuming a triclinic cell, yielded the cell dimensions $a = b = 6.380(1)$, $c = 6.570(1)$ Å, and $\alpha = \beta = \gamma = 90.00(1)^\circ$. The electron-probe analysis (Cabri, 1972) indicated the chemical composition to be $(Pt_{0.64}Pd_{0.27}Ni_{0.14})S_{1.00}$ or approximately $Pt_5Pd_2NiS_8$ when based on the unit-cell content.

The intensities of an asymmetric set of hkl reflexions were measured twice and those of an $hk\bar{l}$ set once, all to a 2θ limit of 126° . Measurements were made on the

4-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation and a $\theta/2\theta$ scan with a 2θ width of 2.0 to 3.0°, according to dispersion. Background counts were measured on each side of the scan for a total time approximating that of the scan (30 sec/degree of 2θ). The intensities of three linearly independent reflexions were recorded every 50 measurements to monitor crystal alignment and instrument stability.

The two independently measured sets of hkl intensity data were corrected for absorption effects using a generalized Gaussian procedure (Gabe & O'Byrne, 1970). Because of the very large absorption coefficient for this material (748 cm^{-1}), it was necessary to check carefully the validity of these corrections using the intensities of equivalent reflexions. Despite careful application of the absorption corrections the overall data reproducibility was 0.066. The corrected hkl intensities were merged and structure factors obtained following application of Lorentz and polarization factors. For the purposes of refinement reflexion was coded as 'observed' at the 10% significance level [*i.e.* $I(\text{net}) > 1.65\sigma(I)$], and 'unobserved' intensities were set equal to $1.65\sigma(I)$. With this criterion, 1475 of the 2297 reflexions were considered observed.

Structure refinement

A trial structure of braggite was determined using Patterson methods and is essentially that reported by Gaskell (1935). The space group $P4_2/m$ was selected for the refinement of braggite because of the absence of significant anomalous scattering effects between the hkl and $hk\bar{l}$ intensities to be expected if the structure were non-centrosymmetric. The metal atoms were located at the special positions $4(j)$, $(0.25, 0.47, 0)$, $2(d)$, $(0, \frac{1}{2}, \frac{1}{2})$, and $2(e)$, $(0, 0, \frac{1}{4})$, and the sulphur atoms at the general position $8(k)$, $(0.31, 0.19, 0.22)$. The distribution of the Harker-vector peak-heights in the Patterson map indicated that there was mostly Pt at sites $2(e)$ and $4(j)$, and Pd at site $2(d)$. On this basis, a comparison of the calculated and observed vector peak-heights showed that the electron density at site $2(e)$ was over-estimated by 10% while that at site $2(d)$ was underestimated by about the same amount. The density at site $4(j)$ was overestimated by some 20%. Although these differences were only of a qualitative nature due to sharpening and thermal-motion effects, they did provide a starting point for determining the occupancies of the metal sites.

Table 1. Refinement of structural models with different metal combinations

Each model was refined with the scattering factors indicated, using three cycles of full-matrix least squares. The final coordinates, isotropic temperature factors ($B = 8\pi^2 U$), and reliability value are given in each case. The R value = $\sum |\Delta F| / \sum |F_o|$.

Model	Site	Scattering factor	x/a	y/b	z/c	$U \times 10^2$	R value
I	$2(d)$	$f(\text{Pd})$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.14 (2)	0.081
	$2(e)$	$f(\text{Pt})$	0	0	$\frac{1}{4}$	0.39 (1)	
	$4(j)$	$f(\text{Pt})$	0.2571 (1)	0.4667 (1)	0	0.42 (1)	
	$8(k)$	$f(\text{S})$	0.3121 (4)	0.1901 (4)	0.2264 (4)	0.28 (3)	
II	$2(d)$	$f(\text{Pd})$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.29 (2)	0.076
	$2(e)$	$\frac{5}{8}f(\text{Pt}) + \frac{1}{8}f(\text{Ni})$	0	0	$\frac{1}{4}$	0.36 (1)	
	$4(j)$	$\frac{5}{8}f(\text{Pt}) + \frac{1}{8}f(\text{Ni})$	0.2571 (1)	0.4667 (1)	0	0.40 (1)	
	$8(k)$	$f(\text{S})$	0.3120 (3)	0.1904 (4)	0.2264 (4)	0.40 (3)	
III	$2(d)$	$f(\text{Pd})$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.29 (2)	0.084
	$2(e)$	$f(\text{Pt})$	0	0	$\frac{1}{4}$	0.56 (1)	
	$4(j)$	$\frac{3}{4}f(\text{Pt}) + \frac{1}{4}f(\text{Ni})$	0.2571 (1)	0.4667 (1)	0	0.29 (1)	
	$8(k)$	$f(\text{S})$	0.3120 (3)	0.1903 (4)	0.2263 (4)	0.45 (3)	
IV	$2(d)$	$f(\text{Pd})$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.29 (2)	0.111
	$2(e)$	$\frac{1}{2}f(\text{Pt}) + \frac{1}{2}f(\text{Ni})$	0	0	$\frac{1}{4}$	NEGATIVE	
	$4(j)$	$f(\text{Pt})$	0.2571 (1)	0.4667 (1)	0	0.58 (1)	
	$8(k)$	$f(\text{S})$	0.3117 (5)	0.1899 (5)	0.2265 (4)	0.38 (4)	
V	$2(d)$	$\frac{5}{8}f(\text{Pt}) + \frac{1}{8}f(\text{Ni}) + \frac{2}{8}f(\text{Pd})$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.99 (2)	0.101
	$2(e)$	$\frac{5}{8}f(\text{Pt}) + \frac{1}{8}f(\text{Ni}) + \frac{2}{8}f(\text{Pd})$	0	0	$\frac{1}{4}$	0.26 (1)	
	$4(j)$	$\frac{5}{8}f(\text{Pt}) + \frac{1}{8}f(\text{Ni}) + \frac{2}{8}f(\text{Pd})$	0.2571 (1)	0.4667 (1)	0	0.28 (1)	
	$8(k)$	$f(\text{S})$	0.3112 (5)	0.1906 (5)	0.2267 (5)	0.42 (3)	

Table 2. Final atomic parameters and standard deviations (in parentheses) for model II

The anisotropic temperature factors are expressed in the form $T = \exp [-2\pi(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \dots)]$. The thermal parameters are multiplied by 10^4 .

	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	$2(d)$	0	$\frac{1}{2}$	$\frac{1}{2}$	30 (3)	26 (3)	31 (3)	-8 (3)	0	0
(Pt, Ni) ₁	$2(e)$	0	0	$\frac{1}{4}$	21 (2)	21 (2)	65 (2)	0	0	0
(Pt, Ni) ₂	$4(j)$	0.2572 (1)	0.4667 (1)	0	45 (2)	32 (2)	42 (2)	-3 (1)	0	0
S	$8(k)$	0.3121 (4)	0.1903 (4)	0.2267 (4)	52 (6)	48 (6)	45 (6)	-4 (5)	-11 (5)	10 (5)

Table 3. Observed and calculated structure factors

Structure factors are listed in blocks of constant hk in columns of l, [F_o] × 10 and [F_c] × 10. The asterisk (*) denotes reflexions considered 'unobserved' at the 10% significance level and an E denotes reflexions corrected for extinction and omitted from the final refinement.

Table with multiple columns containing structure factor data, including observed (F_o) and calculated (F_c) values for various hkl reflections. The table is organized by constant hk values and lists l, [F_o] × 10, and [F_c] × 10 for each reflection.

All calculations used in the refinement of the structure of braggite were performed on a CDC 6400 computer with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic scattering factors were those of Cromer & Mann (1968) and averages of these curves were used in testing the site occupancy. Using the full-matrix structure-factor least-squares program *CRYLSQ*, Pt was initially placed at the sites 4(*j*) and 2(*e*), and Pd at 2(*d*), as suggested by the peak-height considerations. Several cycles of least-squares refinement resulted in an *R* value ($\sum |AF|/\sum |F_o|$) of 0.081. The presence of Ni in the structure was considered by comparing the calculated and observed structure factors for several different metal configurations (see Table 1). Several criteria, besides the minimum *R* value, were used in assessing the validity of a given configuration. One criterion was that, since all metals have a distorted square-planar coordination, their temperature factors are expected to be similar. Another was that no composition of braggite has been reported with more than six Pt or less than two Pd (Cabri, 1972); this is consistent with the 2(*d*) site not containing a significant amount of Pt. The configurations II, III and IV, described in Table 1, are based mainly on the Patterson peak heights which indicate that the electron density at sites 2(*e*) and 4(*j*) are overestimated and that Ni may be present in these sites. In II, the Pt and Ni atoms were disordered over both 2(*e*) and 4(*j*); in III, they were disordered over site 4(*j*) and, in IV, over site 2(*e*) only. In configuration V, the metals were

completely disordered over the three sites. In all these configurations, the site 2(*d*) contains Pd and site 8(*k*) sulphur.

Six cycles of full-matrix least-squares refinement were performed on each configuration, applying isotropic temperature factors and the anomalous scattering corrections of Cromer (1965). The refined parameters showed that configurations IV and V were considered less likely than I, II or III, both because of significantly higher *R* values and because of less reasonable temperature factors. It should also be noted that IV is the only configuration in which Ni is present at the Pd site and that this in turn requires the disorder of Pd over the Pt sites. Added complexity of this type does not appear to be warranted, either from the uniqueness of the Pd site implied on composition grounds, or from the *R* values of configurations I, II, and III. Although the *R* values of I, II and III are similar, the consistency of the temperature factors in I and II makes these two configurations seem more reasonable in view of the similar coordination of the sites. However, there seems to be no apparent reason why Ni should substitute preferentially into 2(*e*) as opposed to 4(*j*), and configuration II appears, therefore, to provide the most reasonable model.

Large structure factors, calculated on the basis of configuration II, showed systematic errors that indicated secondary extinction effects. A plot of I_c/I_o versus I_c was consistent with the empirical relationship $I_c/I_o = \epsilon I_c + K^2$, where the secondary extinction coefficient $\epsilon = 0.18 \times 10^{-4}$ and F_o scale, $K = 0.96$. Appropriate corrections were made to the observed structure factors and these reflexions (26) were excluded from the subsequent refinement. After six cycles of anisotropic refinement, model II converged to an *R* value of 0.068. This value is consistent with the overall data reproducibility of 0.066. The final atomic parameters are given in Table 2 and the observed and calculated structure factors are listed in Table 3.

Description of the structure

The structure of braggite (Fig. 1) is essentially that described for synthetic PdS (Gaskell, 1935) but with some differences in coordination. This basic structure-type has been described by Gaskell as resulting from the combined coordination of square-planar coordinated metals and tetrahedrally coordinated sulphur. Distortions of the 'ideal' geometries, which are observed in the PdS structure, result from a combination of these two quite different coordinations. This explanation seems valid also for the structure of braggite although there are differences between the two structures that enable several important observations to be made. The final atomic thermal parameters, listed in Table 2 and illustrated as thermal ellipsoids in Fig. 1, show thermal motion to be essentially isotropic except for the (Pt, Ni) site 2(*e*), which shows significant anisotropic motion along the *x* axis. This appears to

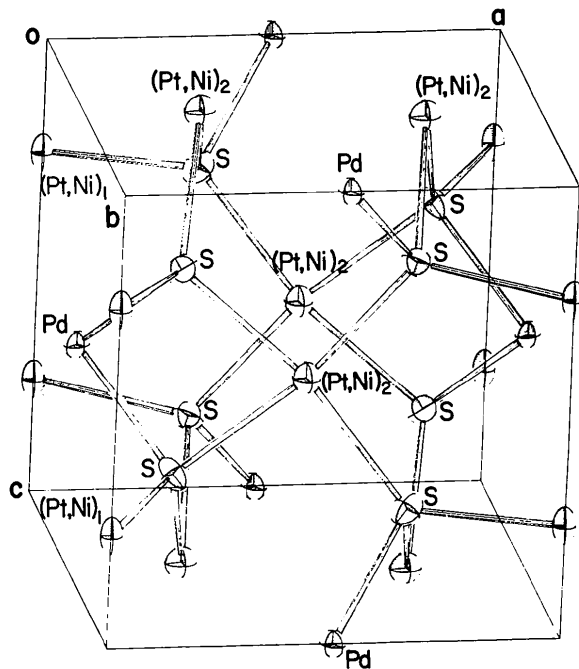


Fig. 1. The structural model of braggite with each atom in a single unit cell represented as a thermal ellipsoid, plotted using *ORTEP* (Johnson, 1965) at the 99% probability limit.

be definitely due to pronounced thermal motion in this direction rather than a disorder effect, although why this should be so is not clear.

In braggite, the sulphur atom is surrounded by a metal tetrahedron [Fig. 2(a)] with angles ranging from 93.7° to 124.2° , while in PdS, the corresponding angles are 95.3 to 119.8° . The metal-to-sulphur distances of Pd-S = 2.26 \AA and $\langle(\text{Pt,Ni})\text{-S}\rangle = 2.33 \pm 0.01 \text{ \AA}$ are in close agreement with those in PdS (2.26 \AA , $2.35 \pm 0.08 \text{ \AA}$, respectively). Although these tetrahedra are distinctly irregular the agreement between the corresponding values in braggite and PdS suggests that the environment of the sulphur is comparable in both structures, and that the Pd 2(d) site in braggite is quite distinct from the (Pt,Ni) sites. The coordination of the Pd 2(d) site is essentially square-planar in both structures [Fig. 2(b)], with edges of 2.98 and 3.41 \AA and central angles of 97.8 and 82.2° in braggite and cor-

responding values of 2.92 and 3.46 \AA , and 99.7 and 80.3° respectively in PdS. This agreement further supports the contention that the 2(d) site in braggite is occupied by Pd atoms.

In contrast, the coordinations of the (Pt,Ni)₁ 2(e) and the (Pt,Ni)₂ 4(j) sites [Fig. 2(c) and 2(d)] both show significant differences between the two structures. Coordination about site 2(e) approaches 'ideal' square-planar in both structures, but the S-S interatomic distance in braggite is $3.31 (1) \text{ \AA}$ and in PdS is 3.43 \AA , emphasizing that this site is occupied by different metal types. The square-planar coordination about the 4(j) site is irregular (edges 2.98 , 3.25 , 3.59 \AA and central angles 79.2 and 101.2°) and in general, different from that of PdS (2.92 , 3.19 , 3.71 \AA and 77.2 , 107.6° respectively). The difference between braggite and PdS in the coordination at sites 2(e) and 4(j) may be expected from the replacement of (Pt,Ni) with Pd.

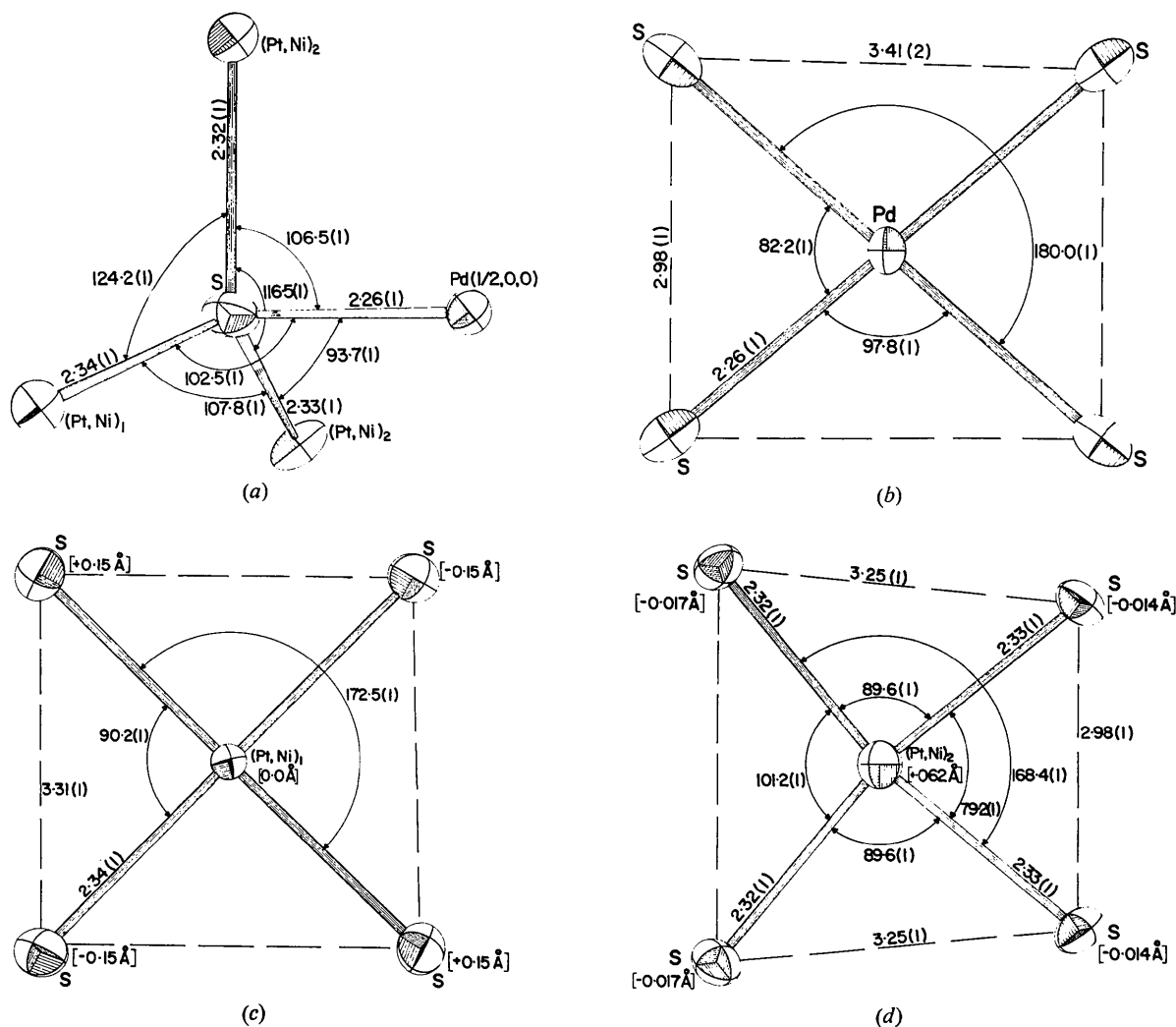


Fig. 2. The interatomic bond distances (\AA) and angles ($^\circ$) involving atoms about each type of braggite. Displacements (\AA) of the atoms from a mean plane are enclosed in square brackets. The atoms are shown as thermal ellipsoids, plotted at a 99% probability limit, about the (a) sulphur site 8(k), (b) Pd site 2(d), (c) (Pt,Ni)₁ site 2(e) and (d) (Pd,Ni)₂ site 4(j).

One may expect, therefore, that these sites would have a tendency towards the geometry of the PtS or cooperite structure. This is, in fact, the case with the 4(*j*) site forming what is essentially a cooperite-like subcell ($a \approx 3.3$, $c \approx 6.6$ Å) within the cell of braggite (see Fig. 1). The cooperite-like subcell is considerably twisted with respect to the braggite cell axes but, nevertheless, this type of coordination is entirely consistent with the placement of (Pt, Ni) atoms at the 4(*j*) site. It also follows that the presence of a cooperite-like subcell supports the placement of Pd atoms at the 2(*d*) sites since these sites are quite distinct from this subcell arrangement. This relationship between the braggite and cooperite structures should contribute to a better understanding of the Pt-Pd-S system.

The authors are most grateful to Dr L. J. Cabri of the Mineral Sciences Division who supplied and microanalysed the braggite crystals. Thanks are also due to J. M. Stewart in the laboratory who performed the

preliminary X-ray photographic survey. One of us (J.D.C.) acknowledges the receipt of a National Research Council of Canada Postdoctorate Fellowship during the tenure of this work.

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Acta Cryst. (1973). **B29**, 1451

The Crystal Structure of the Sesquiterpene (–)-Aristolone

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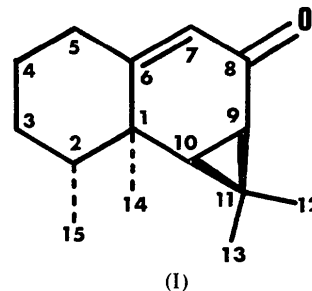
(Received 8 March 1973; accepted 12 March 1973)

Crystals of the sesquiterpene (–)-aristolone, $C_{15}H_{22}O$, are trigonal, space group $P3_2$, $a = 11.782$ (1), $c = 8.286$ (1) Å, $Z = 3$. The structure has been solved by a direct phasing technique using diffractometer data, and refined to $R = 0.055$. The structure solution indicates the sensitivity of the procedure employed to small changes in the criteria for acceptance of new phase indications. A feature of the structure is the hyperconjugation between the cyclopropane ring and an adjacent carbonyl group, resulting in the shortening to 1.439(10) Å of the C(sp^3)–C(sp^2) bond linking the two groups.

Introduction

The sesquiterpene aristolone was first isolated by Kariyone & Naito (1955) from *Aristolchia debilis* Sieb. et Zucc. In a series of papers (Furukawa & Soma, 1961; Furukawa, Oyamada & Soma, 1961; Furukawa, 1961) the molecule was shown to have the chemical formula $C_{15}H_{22}O$ and the structure (I) (which also indicates the numbering adopted in this study). The absolute stereochemistry depicted in (I) is that of (–)-aristolone, determined by indirect correlation with the known absolute configuration of maaliol (Büchi, Greuter & Tokoroyama, 1962). The correctness of the structural assignment was confirmed by the total synthesis of

(±)-aristolone by two independent routes (Piers, Britton & de Waal, 1969a; Berger, Franck-Neumann & Ourisson, 1968).



(I)

The crystal data for (–)-aristolone were first determined (by F. H. A. and J. T.) during a survey of compounds with which the effect of anomalous dispersion

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