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The Crystal Structure of 5-Chloro-1,4-naphthoquinone

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The structure of 5-chloro-1,4-naphthoquinone, $C_{10}H_5O_2Cl$, has been determined from three-dimensional X-ray data by using the 'convolution molecule' method. With positional parameters of the individual atoms and rigid-body thermal parameters the refinement was continued to an R value of 8·45% for 989 independent data (including 169 zero intensities). There are four molecules in a unit cell of dimensions $a=7{\cdot}758$ (10), $b=12{\cdot}845$ (20), $c=8{\cdot}087$ (10) Å, and $\gamma=95{\cdot}6$ (3)°. Space group is $P2_1/b$. $D_x=1{\cdot}551$ g.cm^{-3}. The structure consists of stacks of planar molecules. These are markedly distorted because of the enforced close proximity of the chlorine and one oxygen atom. Details of the molecular geometry are discussed.

Introduction

The molecule of 5-chloro-1,4-naphthoquinone, hereafter abbreviated to 5ClN, is an interesting example of steric hindrance, since through the atoms C(4) and C(5) a close proximity of the chlorine and the one oxygen atom is enforced. Fig. 1 shows the two possible resonance forms of the molecule and the notation used for the atoms. The distance between the atoms C(4) and C(5) is about 2·41 Å in the undisturbed naphthalene molecule. This distance is too short to position the chlorine and oxygen atoms without considerably deforming the electron shells of the two atoms. Thus one would expect the distance between the chlorine and the oxygen atoms to be enlarged and the frame of the carbon atoms to be distorted. To obtain the characteristics of this distortion is one aim of the structure determination.

The structure of 5ClN is also interesting in that it can be compared with several structures of similar molecules: 1,4-naphthoquinone (Gaultier & Hauw, 1965), juglone (Cradwick & Hall, 1971), and naphthazarine (Borgen, 1956; Watase, Osaki & Nitta, 1957; Golder & Zhdanov, 1958; Pascard-Billy, 1962). (In the molecule of juglone the carbon atom C(5) carries a hydroxy group instead of the chlorine atom of 5ClN.) A comparison of the dimensions of the 5ClN molecule with those of several α-halogenated anthraquinone molecules, for which considerable distortions have been reported (for references see Table 3), is also made.

Experimental

5ClN crystallizes from ligroin as yellow needles and sublimes easily. The crystals are monoclinic (we have chosen the c axis as monoclinic axis) and grow prismatically; the axis of the prism is the a axis of the crystal. The {010} faces are the best developed. The lattice constants were determined from Weissenberg films taken about the a axis, from precession films, and with the Weissenberg diffractometer. The crystal data are:

M.W. 192·559; $a=7{\cdot}758\pm0{\cdot}010$, $b=12{\cdot}845\pm0{\cdot}020$, $c=8{\cdot}087\pm0{\cdot}010$ Å, $\gamma=95{\cdot}6\pm0{\cdot}3°$, $V=801{\cdot}51$ Å^3, $Z=4$; $D_x=1{\cdot}551$, $D_m=1{\cdot}595$ g cm^{-3}.

Systematic absences: $k=2n+1$ for $hk0$, $l=2n+1$ for $00l$.

Space group: $P2_1/b$ (C_{2h}^5); one molecule in the asymmetric unit.

The intensities were measured with a Stoe automatic Weissenberg diffractometer. The primary beam was monochromated with a LiF crystal (200 reflexion), $\lambda=1{\cdot}5418$ Å. A total of 1024 reflexions $0kl$, $0\bar{k}l$, $1kl$, $2kl$, $3kl$ and $4kl$ were measured. The crystal used had the dimensions $3{\cdot}5\times0{\cdot}188\times0{\cdot}033$ mm; the faces with lengths 3·5 mm were {010} and {001}. An absorption correction was performed by using the method of Busing & Levy (1957), $\mu=38{\cdot}29$ cm^{-1}. Lorentz and polarization corrections were applied in the usual manner. In order to judge the quality of the intensity measurements we calculated an R value over the two sets of corrected intensities $0kl$ and $0\bar{k}l$. $R(0kl)=0{\cdot}072$ for 113 reflexions, and $R(0kl)=0{\cdot}035$ for the 27 low-angle reflexions in each set. 35 reflexions were removed from the data set because of extinction and the refinement was carried out with 989 independent reflexions, of which 169 were judged to have zero-intensity. Weights were calculated for the refinement from the counting statistics of the peak and background measurements.

Structure determination

Since the dimensions of the 5ClN molecule can be predicted to a sufficient approximation and a chlorine atom is present in the molecule, the 'convolution molecule' method (Hoppe, 1957; Huber, 1965) offered itself as a means of determining the structure. In the initial model of the molecule distances of 1·40 Å for all C–C bonds, 1·23 Å for the C=O bonds, and 1·71 Å for the C–Cl bond were used. The molecule was assumed to be planar. The application of the 'convolution molecule' method was immediately successful. The method yields the orientation of the molecule in a Cartesian reference system (3 Eulerian angles φ, θ, ϱ) and 3 translation parameters (x_0,y_0,z_0) of the fixed origin of the molecule in the unit cell. For the set of positional rigid-body parameters thus obtained, an overall temperature factor of $B=3{\cdot}8$ Å^2, and scale factors derived from intensity statistics, we calculated an R value of 0·432, using only 465 low-angle reflexions. These parameters were then refined as described by Scheringer (1963). After 8 cycles an R value of 0·271 was obtained, the Eulerian angles having changed by less than 0·6°. The large value of R indicated that the parameters used were no longer sufficient with respect to the quality of the data, and errors in the model of the molecule prevented further refinement. Thus we continued the refinement with the positional parameters of the individual atoms (without the hydrogen atoms), and with rigid-body thermal parameters **TLS**, trace (**S**) = 0 (*cf.* Schomaker & Trueblood, 1968). (The structure-factor **TLS** program was written by the author.) After 5 cycles we obtained $R=0{\cdot}104$ for 709 reflexions. Because of extinction, 35 reflexions were removed and 2 more cycles yielded $R=0{\cdot}0732$. Now the high-angle reflexions were added and a further 5 cycles computed. The positional parameters of the hydrogen atoms could not be reasonably refined. Therefore we positioned the hydrogen atoms at the normal distance of 1·09 Å from the carbon atoms in the plane of the molecule. For 989 independent reflexions we obtained $R=0{\cdot}0845$, and $R=0{\cdot}0703$ for the weighted data. If the zero intensities are excluded ($|F_{\text{obs}}|<2{\cdot}5$ on absolute scale) the R value obtained is 0·0729. This corresponds to the quality of our measurements which we assessed from the $0kl$ and $0\bar{k}l$ data. A table of observed and calculated structure factors has been deposited with the National Lending Library as Supplementary Publication No. SUP 30042.* The positional parameters of the atoms and their standard deviations (in parentheses) are given in Table 1, the thermal parameters and their standard deviations in Table 2. (For the parameters of the hydrogen atoms no standard deviations are given.) The final scale factors of the 5 layers are 5·52, 5·42, 5·32, 5·33, and 4·87 (for $4kl$). The good agreement confirms the consistency of our intensity measurements and the correctness of the absorption correction applied.

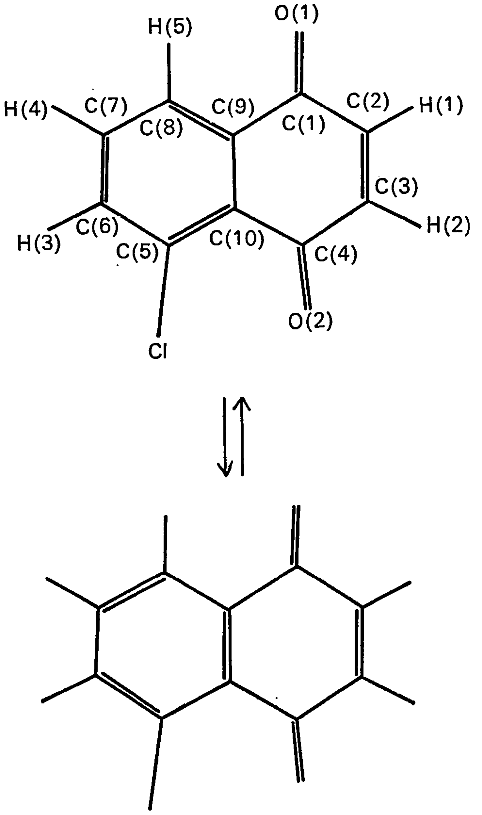

Fig. 1. The two resonance forms of the molecule.

Table 1. *Fractional atomic coordinates*

Standard deviations are given in parentheses.

	x	y	z
C(1)	0·1363 (7)	−0·0381 (5)	−0·2337 (7)
C(2)	0·1940 (7)	0·0606 (5)	−0·3171 (7)
C(3)	0·2855 (7)	0·1371 (4)	−0·2373 (7)
C(4)	0·3256 (7)	0·1319 (4)	−0·0606 (7)
C(5)	0·3304 (7)	0·0115 (4)	0·1886 (7)
C(6)	0·2906 (7)	−0·0878 (4)	0·2629 (7)
C(7)	0·1969 (7)	−0·1654 (4)	0·1754 (7)
C(8)	0·1498 (7)	−0·1487 (4)	0·0157 (7)
C(9)	0·1879 (7)	−0·0499 (4)	−0·0618 (7)
C(10)	0·2800 (7)	0·0309 (4)	0·0253 (6)
O(1)	0·0453 (5)	−0·1058 (3)	−0·3093 (5)
O(2)	0·3894 (5)	0·2094 (3)	0·0095 (5)
Cl	0·4453 (2)	0·1037 (1)	0·3086 (2)
H(1)	0·1975	0·0664	−0·4399
H(2)	0·3436	0·2055	−0·3001
H(3)	0·3473	−0·0952	0·4074
H(4)	0·1771	−0·2405	0·2357
H(5)	0·0334	−0·1989	−0·0405

Table 2. *Rigid-body thermal parameters* **TLS** *referred to crystal axes*

Trace (**S**) = 0.

T^{11}	0·00016 (3)	S_1^1	−0·00026 (19)
T^{22}	0·00023 (1)	S_1^2	0·00043 (13)
T^{33}	0·00057 (1)	S_1^3	−0·00073 (22)
T^{12}	−0·00002 (1)	S_2^1	0·00072 (40)
T^{13}	0·00006 (1)	S_2^2	0·00086 (26)
T^{23}	−0·00002 (1)	S_2^3	0·00374 (44)
L_{11}	0·114 (14)	S_3^1	−0·00435 (39)
L_{22}	0·315 (43)	S_3^2	−0·00112 (26)
L_{33}	0·470 (30)	S_3^3	−0·00060 (32)
L_{12}	−0·097 (17)		
L_{13}	0·066 (14)		
L_{23}	−0·088 (22)		

The values of the rigid-body thermal parameters will be discussed elsewhere (Scheringer, 1973). In order to establish the structural significance of the

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* Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

correlation tensor **S** we have also computed a refinement with parameters $\mathbf{TLx}_0$ ($\mathbf{x}_0$ are the coordinates of the centre of libration, *cf.* Pawley, 1963). The *R* value for this refinement was 0·0904. Since there are only 5 additional parameters involved in the **S** tensor, this tensor proved to be highly significant. (The $\mathbf{TLx}_0$ model could be rejected below the 0·005 level of significance.)

Description of structure

The molecules are packed in piles along the **a** axis; a second pile in the crystal is related to the first by the *b* glide plane. The normal of the plane of the molecule is inclined at 26·54° to the *a* axis. The equation of the plane of the molecule is

$$0{\cdot}895\,x-0{\cdot}312\,y-0{\cdot}320\,z=0\,,$$

where the coordinates are referred to a Cartesian system whose origin is at the centre of gravity of the molecule, and whose axes are parallel to **a**, **b***, **c**. Two molecules in a pile, which are referred to each other by the $\bar{1}$ operation, form half the contents of the unit cell. The arrangement of the molecules in the cell is shown in Fig. 2 (projection along the *a* axis) and Fig. 3 (projection along the monoclinic axis, *c*). Some distances between molecules, which belong to different piles, are indicated in Figs. 2 and 3 as dotted lines. The shortest distances are 2·70 Å for O(2)–H(3), and 2·75 Å for O(2)–H(4). All intermolecular contacts are of the van der Waals type.

The packing of the molecules in the crystal is very similar in the structures of 5ClN, 1,4-naphthoquinone (Gaultier & Hauw, 1965), juglone (Cradwick & Hall, 1971), and naphthazarine, form A (Pascard-Billy, 1962). The similarity between the structures of juglone and naphthazarine (A) has already been pointed out by Cradwick & Hall. The four structures have similar cell dimensions and the same space group $P2_1/c$ ($P2_1/b$, $P2_1/n$). Also, the mean perpendicular interplanar distances and the angles of inclination of the molecular plane with the *a* axis are very similar: 3·47 Å, 26·5° for 5ClN; 3·48–3·55 Å, 31·9° for 1,4-naphthoquinone (Gaultier & Hauw, 1965); 3·41 Å, 21·8° for juglone (Cradwick & Hall, 1971); and 3·4 Å, 23·6° for naphthazarine (A) (*Structure Reports*, 1958). The structures are, however, different with respect to the position of the axes of inclination. For 5ClN the axis coincides almost exactly with the line C(4)–C(6) (the deviation is 1°); for 1,4-naphthoquinone it is approximately along the line C(4)–C(5). On the other hand, for juglone and naphthazarine (A) the axes of inclination are approximately along the bond C(9)–C(10), *i.e.* the angle between the two pairs of inclination axies is approximately 80°. The projections along the *a* axis are still very similar for all four structures because the angles of inclination are small (<32°); *cf.* Fig. 2 with Fig. 4 of Gaultier & Hauw (1965), with Fig. 2 of Cradwick & Hall (1971), and with Fig. 17 of Pascard-Billy

Table 3. *Some geometrical features of the distortions of the molecules as determined for* 5ClN *and six α-halogen derivatives of anthraquinone*

Compound	Distance C(4)–C(10)	Angle C(4)–C(10)–C(5)	Angle Hal–C(5)–C(6)	Sum of the 3 exterior angles at C(4), C(10), C(5) −360°	Distance O(2)–Hal	Sum of van der Waals radii (O(2), Hal)	Out-of-plane distance (Å) O(2)	Out-of-plane distance (Å) Hal	*R* value (%)	Reference
5ClN	1·49 Å	123°	116°	9°	2·83 Å	3·14 Å	−0·19	+0·01	8·4	
1,5-Dichloroanthraquinone	1·44	125	116	9	2·79	3·14	−0·12	−0·18	~16·0	Bailey (1958)
1,5-Dibromoanthraquinone	1·47	126	114	10	2·93	3·33	−0·19	+0·04	16·2	Chetkina & Golder (1957)
1,5-Diiodoanthraquinone	1·50	127	111	8	3·02	3·48	−0·34	+0·17	18·8	
α-Chloroanthraquinone	1·54	125	114	8	2·86	3·14	−0·06	+0·57	18·0	Klimasenko & Golder (1969)
α-Bromoanthraquinone	1·52	127	114	10	2·97	3·33	±0·04	±0·03	13·5	Klimasenko, Golder & Zhdanov (1969)
7,10-Dichloroanthraquinone oxadiazole	1·48	125	116	5	2·80	3·14	+0·20	+0·09	15·9	Mikhno & Chetkina (1972)
	1·50	121	113	6	2·84	3·14	+0·50	−0·52		

(1962).* The projections along the monoclinic axes are, however, notably affected by the different positions of the inclination axes in the two pairs of structures; *cf.* on the one hand Fig. 3 of this work and Fig. 3 of Gaultier & Hauw (1965) with the projections along the *b* axis of juglone and naphthazarine (A) on the other.

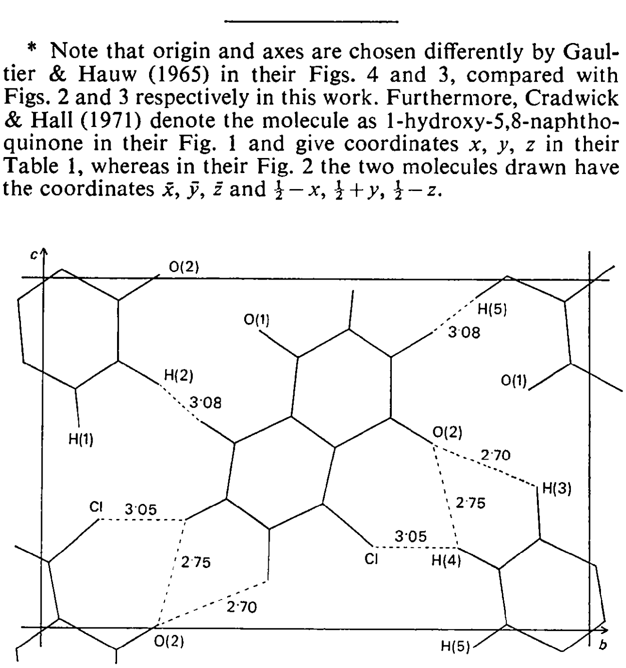

Fig. 2. Projection along the *a* axis. Only the two molecules x, y, z and $x, \frac{1}{2}+y, \frac{1}{2}-z$ are drawn. The shortest intermolecular distances (dotted lines) are given in Å.

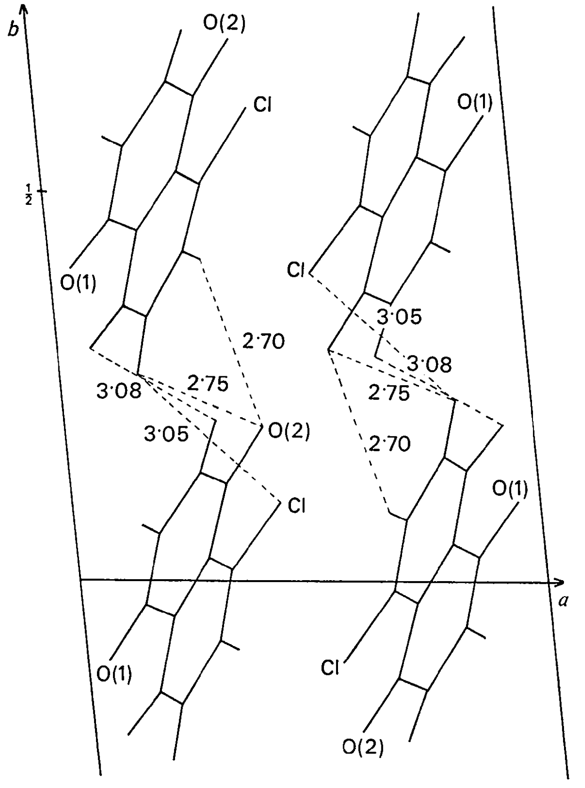

Fig. 3. Projection along the monoclinic axis, *c*. In this projection the lattice constant *b* is reduced to $\frac{1}{2}b$.

We have also determined the crystal data of the structure of 5,8-dichloro-1,4-naphthoquinone. In this structure another principle of arranging the molecules operates in the crystal, for the structure, which is tetragonal, is in the space group $I4_1/a$ and has lattice constants $a=b=30·98$, $c=3·790$ Å, and 16 molecules in the unit cell.

Molecular dimensions

The dimensions of the 5ClN molecule are shown in Fig. 4, except for the positions of the hydrogen atoms. The standard deviations for the C–C and C=O bonds have a maximum value of 0·008 Å and for the C(5)–C(1) bond the standard deviation is 0·005 Å. The standard deviations for the bond angles have a maximum value of 0·53°. The bond-length corrections, which are necessary to account for the effect of thermal motion, were calculated from the rigid-body libration tensor **L**, *cf.* Scheringer (1972). The corrections range from 0·0023 to 0·0067 Å, and thus lie within the limits of the standard deviations of the bond lengths. The maximum value of the corrections, 0·0067 Å, applies to the C(5)–Cl bond. The reason for the small corrections is that the motions of the atoms in the molecule are highly coupled. This gives large values of the diagonal components of the coupling tensors $\mathbf{U}_{rs}$ and thus small values of the corrections; *cf.* Scheringer (1972), equations (3.1), (3.3), and (3.6).

The molecule is essentially planar. The planarity was investigated by a method already described (Scheringer, 1971). Only the carbon atoms were used to determine the 'best' plane. The mean deviation of the carbon atoms from this plane is 0·042 Å, which is about four times the standard deviations. For the atoms O(1), O(2), and Cl the deviations are −0·134, −0·190, +0·008 Å respectively. The deviations of the oxygen atoms from the 'best' plane are more than 10 times the standard deviations and thus they are very likely to be real.

The 5ClN molecule is markedly distorted compared with the naphthalene molecule. Most obvious is the enlargement of the angles O(2)–C(4)–C(10), C(4)–C(10)–C(5), C(10)–C(5)–Cl; they all have values of about 123°; *cf.* Fig. 4. On the other hand, the angle C(8)–C(9)–C(1) is fairly small (118·6°). The single bond C(4)–C(10) (1·489 Å) is the largest in the molecule. Thus the enforced close proximity of the atoms Cl and O(2) has the effect that the molecule is expanded in the region O(2)–C(4)–C(10)–C(5)–Cl. Even so, the distance O(2)–Cl (2·83 Å) is still fairly short. It seems that a compromise is achieved between bending of the valence directions and deformation of the electron shells of the (non-bonded) atoms Cl and O(2).

We compared the distortions found for 5ClN with those that have been reported for some α-halogenated

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* Note that origin and axes are chosen differently by Gaultier & Hauw (1965) in their Figs. 4 and 3, compared with Figs. 2 and 3 respectively in this work. Furthermore, Cradwick & Hall (1971) denote the molecule as 1-hydroxy-5,8-naphthoquinone in their Fig. 1 and give coordinates x, y, z in their Table 1, whereas in their Fig. 2 the two molecules drawn have the coordinates $\bar{x}, \bar{y}, \bar{z}$ and $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

anthraquinones. Some of the geometrical features of the distortions and the *R* values of the refined structures are listed in Table 3, together with the relevant references. The headings in Table 3 refer to the carbon atoms of 5ClN and have to be applied to the anthraquinone molecules accordingly. Although the structures of the anthraquinone derivatives are not very accurately determined, the lengthening of the C(4)–C(10) bond and the enlargement of the exterior angles at the atoms C(4), C(10), and C(5) turn out to be very similar in all the molecules, *cf.* Table 3. The out-of-plane distances for the oxygen and halogen atoms, which are listed in Table 3, refer to the 'best' plane determined from the carbon atoms only. Except for the α-bromo compound, the out-of-plane distance of at least one of the two atoms, oxygen or halogen, is considerable, but no common trend of the out-of-plane distances can be deduced for the seven molecules.

The resonance system of chemical bonding (Fig. 1) in the 5ClN molecule, which is predicted by the chemists, is well confirmed by our structure determination. The double bonds C(1)=O(1) and C(4)=O(2) have normal lengths, 1·23 and 1·21 Å respectively. The same holds for the double bond C(2)=C(3), at 1·33 Å. Also the single bonds C(1)–C(2), C(3)–C(4), C(9)–C(1) have normal lengths, 1·47, 1·47, 1·46 Å respectively, whereas the bond C(4)–C(10) at 1·49 Å appears to be lengthened. In the left carbon ring the sum of the bond lengths C(5)–C(6), C(7)–C(8), C(9)–C(10), at 4·187 Å, does not appear to be significantly shorter than the sum of the bond lengths C(5)–C(10), C(6)–C(7), C(8)–C(9), at 4·211 Å. Since the bonds in the left carbon ring should have nearly the same lengths, the differences in the C–C bonds of this ring probably have to be attributed to experimental errors in the structure determination.

The dimensions of the molecules of 5ClN, 1,4-naphthoquinone and juglone, which have the same resonance system for their chemical bonding, are found to compare reasonably well. For all three molecules the resonance system is essentially confirmed by the structure determinations. But there are notable differences among the corresponding bond lengths. The structure of 1,4-naphthoquinone and juglone are not very accurately determined, however; $R=0{\cdot}13$ for 478 data and $R=0{\cdot}11$ for about 400 data respectively. Thus a comparison of the molecular dimensions is only possible to a limited extent. We have already mentioned the larger bond angles at C(4), C(5), and C(10) for 5ClN. It is remarkable that the notable differences in the bond lengths appear in the region C(7)–C(8)–C(9)–C(1)–C(2), *i.e.* in a region where the molecules should be equal since they are substituted not in this region but at the atom C(5). The four bond lengths in the above sequence of the carbon atoms are

1·37, 1·43, 1·46, 1·47 Å for 5ClN
1·41, 1·39, 1·43, 1·48 Å for 1,4-naphthoquinone
1·42, 1·36, 1·51, 1·51 Å for juglone.

The differences among the corresponding bonds are larger than the calculated standard deviations but are probably ascribable to experimental errors in the structure determinations. Furthermore, for juglone the unusual lengths of the bonds C(1)=O(1), at 1·20 Å, and C(4)=O(2), at 1·26 Å, may be mentioned, whereas in 5ClN and 1,4-naphthoquinone these bonds all have the same (normal) lengths (1·21 to 1·23 Å). Perhaps, in juglone the C(4)=O(2) bond is weakened by an intramolecular hydrogen bond O(3)–H···O(2).

The resonance system for the chemical bonding of the naphthazarine molecule differs from that of 5ClN because in the crystal, naphthazarine is centrosymmetric, which makes further resonance forms possible in the molecule. This agrees well with the differences

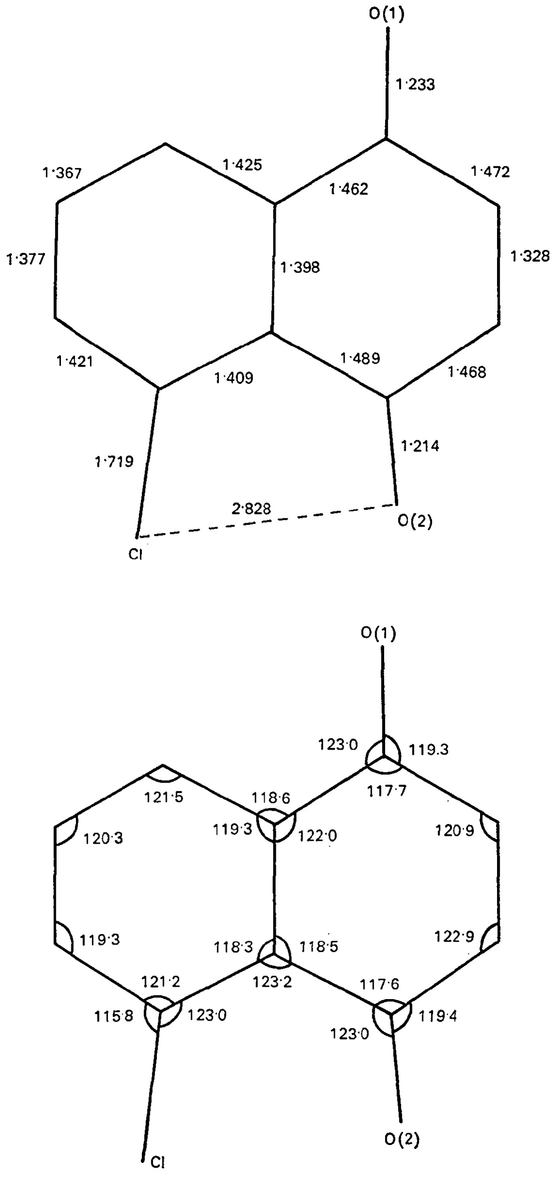

Fig. 4. Bond lengths (Å) and angles (°).

of some bond lengths found with the structure determinations (*Structure Reports*, 1962). In naphthazarine the C–O distances, 1·30 to 1·33 Å, are longer than in 5ClN, which can be ascribed to the partial loss of the quinonoid double bonding. Similarly, the bonds C(2)–C(3) (1·38 Å) and C(9)–C(10) (1·46 Å) are lengthened in the naphthazarine molecule as compared with 5ClN.

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The Crystal Structure of Silver Sodium Sulphite Dihydrate $AgNaSO_3.2H_2O$

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The crystal structure of silver sodium sulphite dihydrate, $AgNaSO_3.2H_2O$, has been determined from three-dimensional X-ray diffractometer data. The unit cell is triclinic, space group $P\bar{1}$, with the following dimensions: $a=5·949$ (5), $b=9·277$ (9), $c=5·465$ (3) Å, $\alpha=101·06$ (8), $\beta=90·65$ (6), $\gamma=117·29$ (6)°. There are two formula units in the cell. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to an R value of 0·067 for 727 observed reflexions. The silver atom is nearly linearly coordinated by the sulphur atom and one of the sulphite oxygen atoms; thus results a chain-like structure for $AgSO_3^-$. The Ag–S and Ag–O distances are 2·474 (4) and 2·194 (9) Å respectively. Sodium is octahedrally coordinated by three sulphite oxygen atoms and three oxygen atoms belonging to water molecules; the average Na–O distance is 2·418 Å. The average dimensions of the sulphite ion are: S–O distance 1·522 Å and O–S–O angle 106·3°.

Introduction

The crystal structures of Na_2SO_3 (Larsson & Kierkegaard, 1969) and Ag_2SO_3 (Larsson, 1969) have previously been determined at this Institute as a part of a larger program concerning the structural chemistry of metal sulphites. A recent report (Kierkegaard, Larsson & Nyberg, 1972) gives a general discussion of the structural aspects of sulphites so far studied by X-ray methods.

The present investigation was undertaken to elucidate the crystal structure of the double sulphite of sodium and silver. The existence of such a phase, with formula $AgNaSO_3.2H_2O$, has been reported in the early literature (Svensson, 1869) but later doubts have been ex-

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