

Molecular Structure of *Cyclooctatetraene* Dimers. I. The 1:1 Silver Nitrate Adduct of the Dimer which melts at 38.5 °C.

By S. C. NYBURG AND J. HILTON

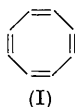
Department of Chemistry, University College of North Staffordshire, Keele, Staffs, England

(Received 10 March 1958 and in revised form 14 July 1958)

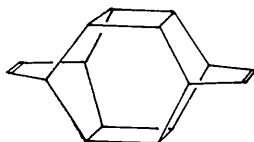
The 1:1 silver nitrate adduct of the *cyclooctatetraene* dimer which melts at 38.5 °C. has been subjected to three-dimensional X-ray analysis. The crystals, normally twinned, belong to the monoclinic system $a = 10.9$, $b = 7.4$, $c = 18.1$ Å, $\beta = 114^\circ$, space group $P2_1/c$ with four molecules to the unit cell. It is shown that the molecule has a structure different from those proposed on chemical grounds.

1. Introduction

Reppe *et al.* (1948) have shown that when *cyclooctatetraene*, (I), is subjected to prolonged boiling



under reflux in an atmosphere of nitrogen, a viscous liquid is obtained which consists largely of a dimer, $C_{16}H_{16}$, which has two double bonds. Reppe *et al.* (1948) assumed that the reaction was of a type which certain unsaturated organic compounds undergo (Diels–Alder reaction) and by analogy suggested that this dimer of *cyclooctatetraene* should have one of two possible molecular structures (II) or (III). Lord & Walker (1954) examined the vibrational spectrum of the liquid and found that neither (II) nor (III) could account



satisfactorily for the spectroscopic data; the balance of evidence favoured (II). Meanwhile Jones (1953) showed the liquid dimer to be impure and obtained from it, via the 1:1 silver nitrate adduct, a colourless crystalline dimer, m.p. 38.5 °C.

Cyclooctatetraene can be made to yield other dimers by varying the conditions of the reaction. One of these, also originally obtained by Reppe *et al.* (1948), contains three double bonds and has been shown by Jones (1953) to yield two different adducts with silver nitrate and, when purified, to melt at 41.5 °C. Jones (1955) has since shown that if the dimerization temperature of *cyclooctatetraene* is kept as low as 100 °C. one or possibly two further dimers are obtained.

Molecular structures have been put forward for all these dimers but we shall not discuss them here.

Since the elucidation of the molecular structure of these dimeric materials by chemical or spectroscopic methods is difficult, we have embarked on a programme of X-ray structure analyses of them and of certain compounds related to them.

2. Preliminary investigation

Preliminary crystallographic studies were concentrated on the dimer itself, crystals of which were kindly supplied by Dr W. O. Jones. However, no immediate progress could be made with this dimer which was abandoned in favour of the 1:1 silver nitrate adduct. Because of the presence of silver and the molecular complexity of the dimer, it proved impossible to unravel the crystal structure from two-dimensional data alone. A full three-dimensional analysis proved necessary.

Colourless crystals of the 1:1 silver nitrate adduct, also kindly supplied by Dr W. O. Jones, were poorly formed and largely without any definite faces. One fragment was oriented about the x -axis by X-rays but the Weissenberg photograph of this could not be interpreted in terms of any known space group. Weissenberg x -axis photographs of a second fragment showed the first to have been a twin with x as the twinning axis and 49° between z -axes. From the second fragment the crystallographic data were found to be:

System, monoclinic. Space group, $P2_1/c$.

$a = 10.9$, $b = 7.4$, $c = 18.1$ Å; $\beta = 114\frac{1}{2}^\circ$.

Density, 1.9 g.cm.⁻³; calculated for four molecules per unit cell, 1.89 g.cm.⁻³.

During exposure to X-rays this crystal and all subsequent crystals, originally colourless, gradually turned black. This blackening did not appear to be accompanied by any serious deterioration of the X-ray photographs except for one crystal which became amorphous after subjection to prolonged exposure.

X-ray examination of many other fragments showed them all to be twinned. The second fragment was the only single crystal we were to find.

3. Nature of the twinning

Small batches of the crystalline material were recrystallized from ethanol (in specimen tubes previously boiled in nitric acid) in the hope of producing well formed single crystals. However, over a wide range of crystallizing temperatures and concentrations the only crystals of useful size obtained were twinned and had the unusual habit shown in Plate I(a). These crystals, which show uniform extinction between crossed polaroids (Plate I(b)) have crystallographic axes disposed as in Fig. 1(a). Fig. 1(b) shows how two

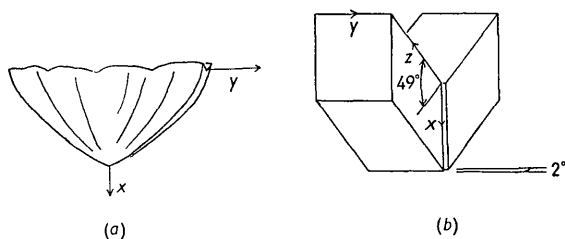


Fig. 1. Arrangement of axes in twinned crystals.

unit cells of the twinned crystal are disposed, the axes being orientated in the same directions as for the crystal in Fig. 1(a). The x -axes of the two twins are parallel and this causes the z -axes to subtend a calculated angle of $2\beta - 180^\circ = 49^\circ$, the effect noted above with the first and all subsequent twinned crystals. The y -axes of the two twins were not quite parallel in any of the specimens which were examined, the angle subtended being always close to 2° (Fig. 1(b)). Hence spots on x -axis Weissenberg photographs were duplicated in pairs 2° apart. There are no obvious simple crystallographic reasons for this twinning. The reason for the 2° angle between y -axes is particularly obscure. We may note however from the scale drawing of Fig. 2

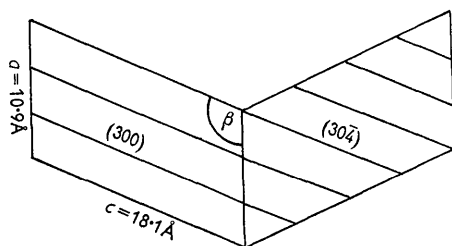


Fig. 2.

that the planes (300) of one crystal almost coincide with the (304) planes of the other. This coincidence proved troublesome during the indexing of reflections (see below).

4. Two-dimensional projections

Intensity data for the $h0l$ projection were obtained from the single-crystal fragment and, utilizing the Patterson projection in the usual way, the fractional co-ordinate of the silver ion assessed as approximately $x_{Ag} = 0.177$ and $z_{Ag} = 0.304$. The resolution of the carbon atoms on the resulting Fourier projection was insufficient for any conclusions concerning molecular structure to be made. The $hk0$ zone of the single-crystal fragment was similarly examined and the Patterson function implied $x_{Ag} = 0.185$ and $y_{Ag} = 0.25$. The electron-density projection for this zone had even the silver ions badly resolved.

5. Three-dimensional data

The single-crystal fragment was used for recording equi-inclination Weissenberg photographs of the $h1l$, $h2l$ and $h3l$ layers. The layers $k = 4$ and 5 lay beyond the range of the camera and the remaining reflections were recorded on oscillation photographs about the x -axis. Unfortunately, during its transfer, the crystal was lost and since no other single-crystal fragments were available, either among the original fragments or among those deposited on recrystallization, a twinned crystal had to be used. It is necessary to examine how three-dimensional data can be obtained from these twins. Fig. 3 shows the disposition of axes in reciprocal

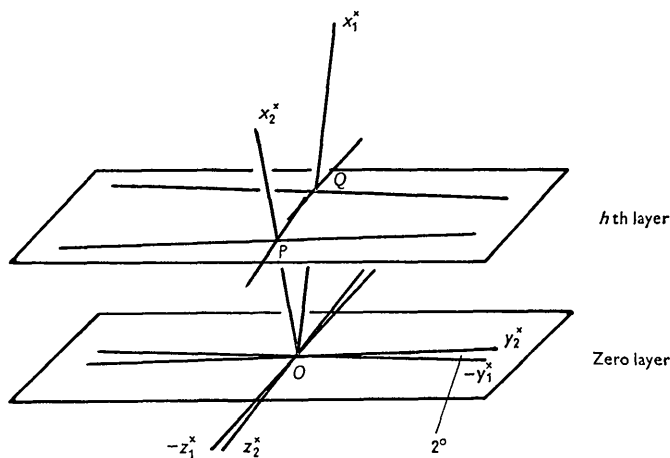


Fig. 3. Arrangement of twinned axes in reciprocal space.

space, with origin O , drawn in the same orientation as Fig. 1(b). These axes are designated by subscripts 1 and 2 to distinguish between each twin. The 2° angle, which has been exaggerated for clarity, causes equivalent reflections from the two twins to be slightly separated on Weissenberg photographs. They are not, of course, separated on oscillation photographs, except in those rare instances where one of the pair lies inside the oscillation range and the other outside it. However, because of the divergence of x_1^* and x_2^* , the reflections are in general resolved on layers other than

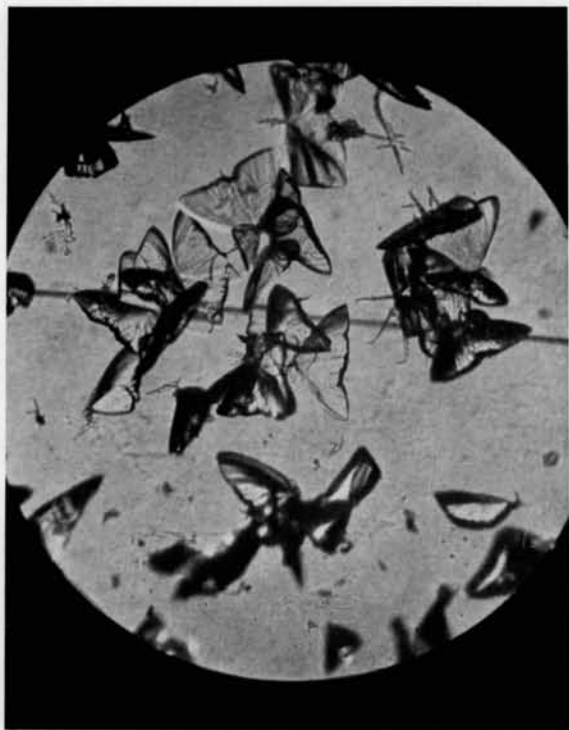


Plate I(a). Twinned crystals in normal view.



Plate I(b). The same between crossed polaroids.

$h = 0$ except for inevitable chance coincidences. On $h = 3$, however, the distance $PQ = 6a^* \cos \beta = 0.386$ lies close to $4c^* = 0.374$, a fact which is expressed differently by the close concurrence of planes (300) and (30 $\bar{4}$) of different twins (Fig. 2). This layer therefore is similar to that for $h = 0$ in that all the reflections occur in unresolved pairs.

By matching resolved reflections from the twinned crystal with those from the single crystal it was possible to estimate the ratio of the volumes of the two twins. This ratio was equal to unity within experimental error. Twenty-two of the intensities required to complete the three-dimensional data were in eleven unresolved pairs. The intensities of these unresolved reflections were apportioned in the ratio of intensities calculated on the basis of silver-ion contributions alone.

The fractional co-ordinate y_{Ag} , suggested by the Patterson function was approximately 0.25. This should result in no silver contribution to reflections hkl with l odd. These reflections were not observed to be especially weak and since the Patterson vector peaks for y close to 0.25 are difficult to resolve, another criterion for establishing y_{Ag} was used. The co-ordinates x_{Ag} and z_{Ag} were assumed to be approximately correct and all the structure factors $F(h2l)$ which could be unambiguously indexed were estimated. Those for l even were divided by $|f_{Ag} \cos 2\pi(hx_{Ag} + lz_{Ag})|$ to give $|\cos 2\pi 2y_{Ag}|$ and those for l odd by $|f_{Ag} \sin 2\pi(hx_{Ag} + lz_{Ag})|$ to give $|\sin 2\pi 2y_{Ag}|$. From these an average value of $|\tan 2\pi 2y_{Ag}|$ was derived and hence possible values of y_{Ag} . The reflections $h3l$ were similarly examined and the value of y_{Ag} compatible with

both found to lie in the range 0.16 to 0.20. This gave a tentative value for y_{Ag} which was later refined by line syntheses and, in part, by optical transforms. The final co-ordinate $y_{Ag} = 0.156$ was used to apportion the intensities of the unresolved reflections.

6. Three-dimensional electron-density data

The observed structure factors were brought to an approximately absolute scale by Wilson's (1942) method and the phases of these calculated on the basis of the silver-ion contributions only. Sections of electron density namely at $y = 0, \frac{1}{4}$ and $\frac{1}{2}$ were computed using hand calculating machines. Although some carbon atoms were clearly resolved, these sections did not allow an unambiguous assignment of carbon positions to be made. Accordingly a complete three-dimensional electron-density computation was deemed necessary.

The electron density was computed throughout the

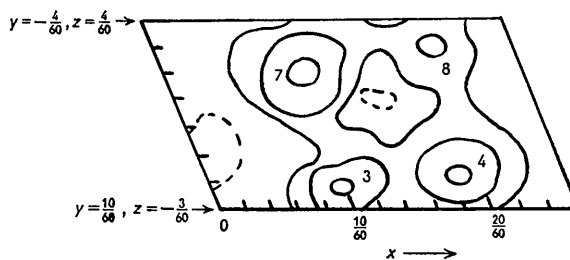


Fig. 4. Section passing close to cyclobutane ring (contours in electrons $\times \text{\AA}^{-3}$).

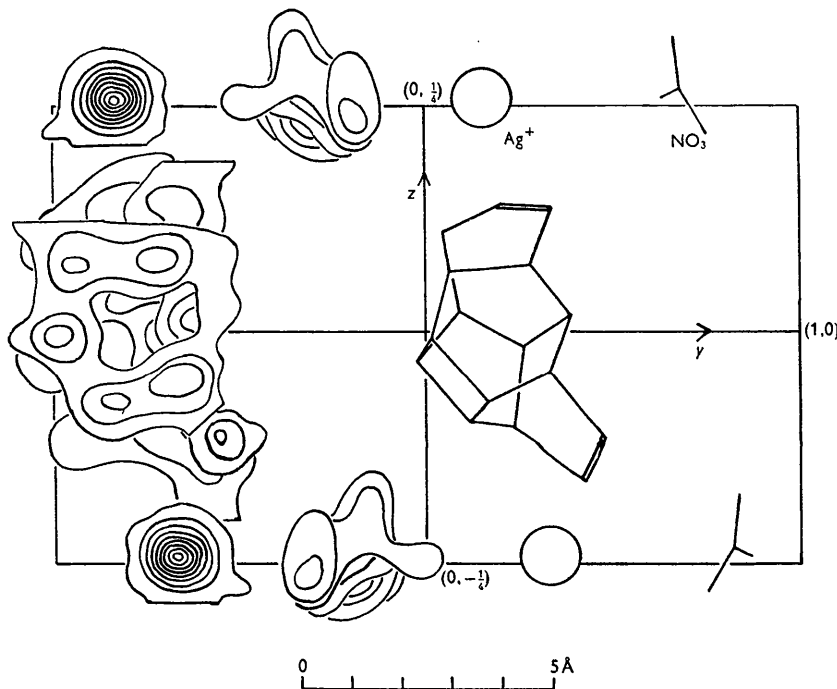


Fig. 5. Composite view of half cell depth, viewed along x^* -axis.†

† Nyburg & Hilton (1957); reproduced by permission from *Chemistry and Industry*.

Table 3. *Observed and calculated structure factors*

F_c are as obtained from Deuce subsequently corrected for temperature factor. All F values are half absolute. F_c values whose calculated phases differ from those used in the Fourier summation are asterisked.

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
002	52	-58.0	20 $\bar{4}$	58	+46.0	012	—	+10.5	044	—	-26.7
4	54	+58.8	$\bar{6}$	94	-65.1	3	18	+26.7	5	—	-1.4
6	20	+10.7	$\bar{8}$	66	+41.2	4	21	-42.4	6	8	-9.7
8	44	-35.0	$\bar{10}$	10	-27.4	5	18	-25.4	7	15	+11.8
10	31	+24.5	300	59	-75.0	6	49	-54.5	8	8	+12.7
12	7	-12.9	2	10	+40.9	7	25	+29.9	9	10	-9.8
100	52	+50.0	4	16	-4.8	8	7	-9.1	10	7	-14.0
2	34	-32.6*	6	33	-25.4	9	—	-4.4	051	7	-3.7
4	46	-34.3	8	13	+17.4	10	8	+0.4*	2	10	-14.2
6	87	+55.4	10	5	-15.5	11	11	-8.6	3	7	+0.9
8	16	-11.7	$\bar{2}$	44	+57.5	12	16	+13.5	4	18	+23.2
$\bar{2}$	62	-61.9	$\bar{4}$	13	-13.9	13	—	+0.4	5	—	-2.7
$\bar{4}$	84	+72.6	$\bar{6}$	34	-31.0	14	13	-6.8	6	8	-14.7
$\bar{6}$	79	-42.1	$\bar{8}$	46	+31.5	15	11	-7.1	110	115	-101.1
$\bar{8}$	15	-17.6	$\bar{10}$	43	-33.8	020	33	-37.3	210	13	-11.9
$\bar{10}$	25	+28.6	$\bar{12}$	21	+16.9	1	57	-65.2	310	16	+8.6
$\bar{12}$	20	-29.4	400	30	-34.7	2	41	+45.5	410	79	+43.4
200	89	-129.5	2	25	-24.1	3	26	+28.4	510	43	+37.8
2	59	+72.5	4	41	+43.4	4	11	-12.1	610	16	-12.5
4	67	-70.0	6	38	-47.0	5	10	+10.0	710	23	-20.2
6	33	+38.3	60 $\bar{2}$	8	-11.5	6	3	-4.7	120	15	-18.7
8	10	+12.2	$\bar{4}$	36	+19.7	7	21	-19.4	220	—	+15.7
10	5	-17.3	$\bar{6}$	—	+15.2	8	3	-2.5	320	26	+30.1
40 $\bar{2}$	12	+35.5	$\bar{8}$	15	-30.9	9	23	+25.4	420	—	+11.4
$\bar{4}$	77	-71.1	$\bar{10}$	18	+27.2	10	18	-10.7	520	16	-13.8
$\bar{6}$	61	+44.4	$\bar{12}$	16	-15.6	11	15	-14.5	620	—	-6.3
$\bar{8}$	33	-11.3	700	8	-2.2*	031	31	+26.8	130	28	-31.2
$\bar{10}$	25	-19.8	2	15	+11.7	2	7	+8.0	230	18	-12.3
$\bar{12}$	15	+14.5	4	8	-14.6*	3	25	-35.1	330	10	+17.8
$\bar{14}$	5	-10.5	6	11	+16.7	4	—	-1.1	430	7	+12.0
500	47	+47.1	$\bar{2}$	8	-17.6	5	33	+43.8	530	—	+2.0
2	25	-25.1	$\bar{4}$	16	+31.0	6	20	+14.6	630	—	-0.9
4	21	+29.3	$\bar{6}$	25	-14.0	7	21	-25.8	730	—	-4.0
6	5	-13.9	$\bar{8}$	23	+17.2	8	—	+1.3	140	15	-19.3
8	5	+2.0*	$\bar{10}$	5	+10.6	9	—	+5.1	240	13	+8.2
50 $\bar{2}$	8	-1.7	$\bar{12}$	15	-11.4	10	—	-7.5	340	29	+22.6
$\bar{4}$	15	-40.0	$\bar{14}$	7	+7.0	11	16	+9.3	440	—	+6.8
$\bar{6}$	43	+52.1	80 $\bar{2}$	5	-0.5*	12	—	-0.3	540	—	-7.2
$\bar{8}$	36	-33.7	$\bar{4}$	5	+8.3	13	18	-8.1	150	15	+22.2
$\bar{10}$	23	+21.2	$\bar{6}$	25	-25.4	14	—	-1.6	250	18	+16.8
600	36	+45.5	$\bar{8}$	18	+18.3	15	15	+7.6	350	5	-7.9
2	3	-18.9	$\bar{10}$	7	-7.8	040	11	-29.1	450	16	-19.0
4	7	-4.0	$\bar{12}$	7	+0.9	1	13	+29.0			
6	15	+11.0				2	7	+20.6			
8	8	-12.0				3	20	-27.4			
20 $\bar{2}$	44	-36.8	011	—	0.0						

asymmetric unit at intervals of $x = 1/30$, $y = 1/30$ and $z = 1/60$ of unit-cell edges on Deuce at the National Physical Laboratory. The programme used was that designed by Dr J. S. Rollett for $P2_1/c$. The hand-calculated values were used to cross-check the machine-computed values at common points.

From contoured plots of these electron-density values the positions of all the atoms were unambiguously assignable except those of the nitrate group. To make quite certain that no errors in identifying adjacent bonded carbon atoms had been made, many oblique sections were plotted out. One such, showing the *cyclobutane* ring, is given in Fig. 4. Although these maps show inevitable false detail, there were no spurious peaks or depressions exceeding $1 \text{ e.}\text{\AA}^{-3}$, except in the immediate vicinity of the silver ion and at the site of the unresolved nitrate group.

7. Structure factor calculations

The temperature factor estimated from Wilson's method was $B = 4.2 \text{ \AA}^2$. When the positions of all atoms had been assessed from the three-dimensional electron-density plot, the structure factors were calculated on the Deuce computer at the English Electric Co., Stafford, to a programme devised by Dr J. S. Rollett. In these calculations the Thomas-Fermi scattering curves for all atoms with $B = 4.2 \text{ \AA}^2$ were used, silver being taken as completely ionic. A plot of $\ln F_o/F_c$ against $\sin^2 \theta/\lambda^2$ gave a new scaling factor for F_o and indicated a temperature factor of $B = 6.7 \text{ \AA}^2$. The F_o and Deuce values were corrected accordingly and those for the principal zones are given in Table 3. (The full table can be obtained from the authors.)

The residual calculated on the basis of silver ions

only was 0.39 with non-observed reflections excluded. When all atoms are included the residual falls to 0.29. If F_c for non-observed reflections are included the residual is 0.37. The true residual must lie between these values and probably fairly close to 0.30. The high residual is in part due to lack of refinement, but is also due to the extremely poor nature of the experimental data. Crystals could not be obtained of a size and shape which would ensure freedom from absorption errors and the reflections themselves were of very poor quality.

8. The crystal structure

(a) The dimer

A composite view of half the unit-cell content seen along the x^* -axis showing relevant layers of the electron-density plot is given in Fig. 5. This projection has certain chemical bonds coincident and the molecular configuration is made clearer in Fig. 6, which shows the numbering scheme adopted. The molecule is seen to differ from those (II) and (III) proposed on chemical grounds.

The silver ions could be precisely located but the positions of the carbon atoms and in particular, of the nitrogen and oxygen atoms, are subject to considerable error. Accordingly, although the co-ordinates

Table 1. Fractional atomic coordinates

Atom	x	y	z
C ₁	0.213	0.466	-0.054
C ₂	0.321	0.426	-0.072
C ₃	0.151	0.142	-0.033
C ₄	0.298	0.108	-0.025
C ₅	0.160	0.338	-0.008
C ₆	0.390	0.277	-0.006
C ₇	0.189	0.007	0.034
C ₈	0.339	-0.014	0.052
C ₉	0.226	0.385	0.081
C ₁₀	0.350	0.304	0.069
C ₁₁	0.191	0.068	0.116
C ₁₂	0.174	0.270	0.131
C ₁₃	0.339	0.034	0.182
C ₁₄	0.264	0.324	0.219
C ₁₅	0.358	0.196	0.232
C ₁₆	0.390	0.128	0.124
Ag ⁺	0.176	0.156	0.304
N	0.161	0.824	-0.193
O ₁	0.096	0.760	-0.259
O ₂	0.274	0.876	-0.175
O ₃	0.113	0.838	-0.145

quoted for these atoms in Table 1 are given to 0.001 of unit-cell edges, the last digit cannot be relied upon.

Fig. 6 shows the C-C bond lengths calculated from the co-ordinates of Table 1. No significance is to be attached to differences between these bond lengths and those (1.54 and 1.33 Å) normally found for single and double bonds. No attempt has been made to rationalize the positions of any of the atoms although certain slight movements away from observed peaks would clearly bring some bond lengths and angles

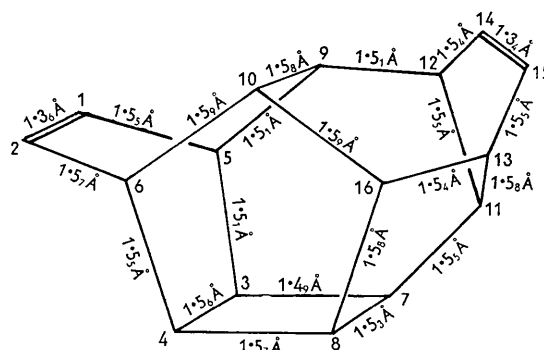


Fig. 6. The dimer molecule.

more closely into line with usual values. We have preferred to set aside the question of the more precise molecular parameters until such time as an accurate X-ray analysis of the dimer itself can be carried out.

None of the exocyclic rings is coplanar. The double bond systems C₅C₁C₂C₆ and C₁₂C₁₄C₁₅C₁₃ are planar within the limits of accuracy. The molecule has no symmetry and is present in the crystal in enantiomorphously related pairs. These are arbitrarily design-

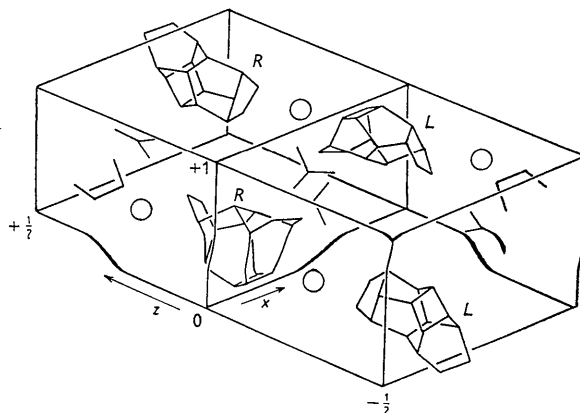


Fig. 7. One unit cell of the crystal structure.

nated *R* and *L* in Fig. 7 which shows one unit cell of the crystal structure.

(b) The silver ion double bond interaction

Each silver ion appears to be closely associated with two double bonds of different dimer molecules. Figs. 8(a) and (b) give in perspective the distances of the double bond mid-points to the silver ion and the angles subtended. The distances and angles involved are similar to those found in complexes of palladium chloride with styrene (Holden & Baenziger, 1955) and with ethylene (Dempsey & Baenziger, 1955). In the ethylene complex the positions of the hydrogen atoms are not known but in the styrene complex the ethylenic carbon-hydrogen bonds must lie in a plane almost normal to the line joining the palladium ion to the mid-point of the double bond. A similar orientation

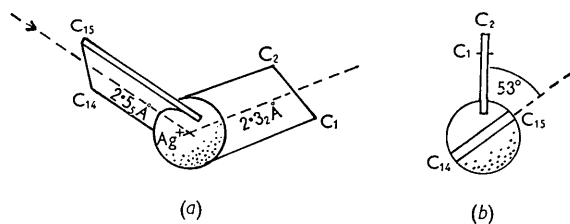


Fig. 8. (a) Silver ion and adjacent double bonds viewed along the y -axis. The broken lines lie in the plane of the diagram and subtend 124° at the silver ion. (b) As (a) viewed along the direction of the arrow.

is present in this crystal structure. The nature of the bonding is uncertain. Chatt & Duncanson (1953) have proposed that in complexes of this type hybridized dp -orbitals of the transition ion overlap with the antibonding π -orbitals of the double bonds. In the present case it is possible to imagine the bonding as originating from the donation of the four π -bond electrons from the two double bonds to the unfilled p -orbitals of the silver ion. These could then form two dp -type hybrid bonds followed by electron redistribution in response to electronegativity differences. If X denotes the axis joining the silver ion to the centre of one double bond the hybrid would be compounded of d_{xz} and p_z . The other hybrid would be compounded of d_{xy} and p_y . However, this would require both the angles shown in Figs. 8(a) and (b) to be 90° instead of 124° and 53° . It can only be assumed that the bonds actually formed represent a compromise between the conflicting requirements of strong bond formation and efficient packing. However, one must not lose sight of a simple polarization effect between the silver ion and the π -bonds being responsible for the observed structure.

(c) Intermolecular distances

The separation between non-bonded carbon atoms is nowhere less than 3.6 \AA . The shortest two silver-nitrogen distances are 3.56 and 3.85 \AA . The crystal

Table 2. Carbon-oxygen interatomic distances

Co-ordinates of dimer molecule	Carbon atom	Oxygen atom	Distance
$x, 1\frac{1}{2}-y, z-\frac{1}{2}$	C_{14}	O_2	2.91 \AA
$x, y+1, z$	C_3	O_3	2.93
$x, y+1, z$	C_4	O_2	3.13
x, y, z	C_1	O_3	3.16

structure of silver nitrate itself does not appear to be known but the nitrate ion is generally regarded to approximate to a sphere of radius 2.3 \AA and the radius of the silver ion is about 1.1 \AA . The disposition of the nitrate and silver ions are compatible with these requirements. Poor resolution probably accounts for some rather short carbon-oxygen interatomic distances. Table 2 gives the shortest four. The distance of 3.01 \AA recorded for a carbon to oxygen separation in *cyclotetramethylene tetranitramine* (Eiland & Pepinsky, 1955) is, however, comparable.

This work was carried out in part-fulfillment by one of us (J. H.) of the requirements for the Ph.D. (Manchester) degree. It is a pleasure to acknowledge the help given at various stages of the work by Prof. H. Lipson, F.R.S. and members of his staff at the Manchester College of Science and Technology and by J. S. Rollett in connection with his programme for Deuce.

The structure-factor calculations performed on Deuce at the English Electric Co., were made possible by the generous help given by Mr W. E. Scott (Director of Research) and by Mr M. R. Wetherfield, who operated the machine.

An award from the Department of Scientific and Industrial Research to cover part of the cost of the computations and a maintenance award to one of us (J. H.) from the Cheshire Education Committee are both gratefully acknowledged.

References

- CHATT, J. & DUNCANSON, L. A. (1953). *J. Chem. Soc.* p. 2939.
 DEMPSEY, J. N. & BAENZIGER, N. C. (1955). *J. Amer. Chem. Soc.* **77**, 4984.
 EILAND, P. F. & PEPINSKY, R. (1955). *Z. Kristallogr.* **106**, 273.
 HOLDEN, J. R. & BAENZIGER, N. C. (1955). *J. Amer. Chem. Soc.* **77**, 4987.
 JONES, W. O. (1953). *J. Chem. Soc.* p. 2036.
 JONES, W. O. (1955). *Chemistry and Industry*, p. 16.
 LORD, R. C. & WALKER, R. W. (1954). *J. Amer. Chem. Soc.* **76**, 2518.
 NYBURG, S. C. & HILTON, J. (1957). *Chemistry and Industry*, p. 1072.
 REPPE, W., SCHLICHTING, O., KLAGER, K. & TOEPFEL, T. (1948). *Liebigs Ann.* **560**, 1.
 WILSON, A. J. C. (1942). *Nature Lond.* **150**, 152.