

THE CHEMISTRY OF THE BROMINATED DERIVATIVES
AND THE CRYSTALLOGRAPHIC DETERMINATION OF THE
STRUCTURE OF THE TETRABROMINATED DERIVATIVE
OF THE C₄-PHOTODIMERS OF 1, 4-NAPHTHOQUINONE

by

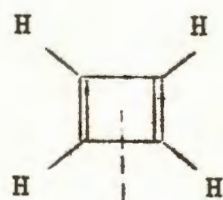
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the degree of Master of Science in the Department of
Chemistry, Potchefstroom University for Christian Higher
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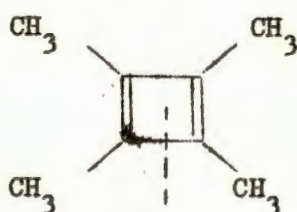
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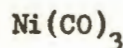
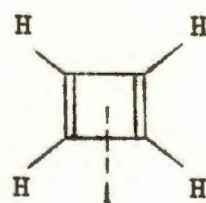
Several attempts were made in the past to synthesize a cyclobutadiene by means of the dehalogenation of tetrahalogenated cyclobutanes. Owing to the instability of cyclobutadiene all these attempts failed, and only in three cases could stable complexes (I¹⁾, II²⁾, III³⁾) with metal salts be isolated.



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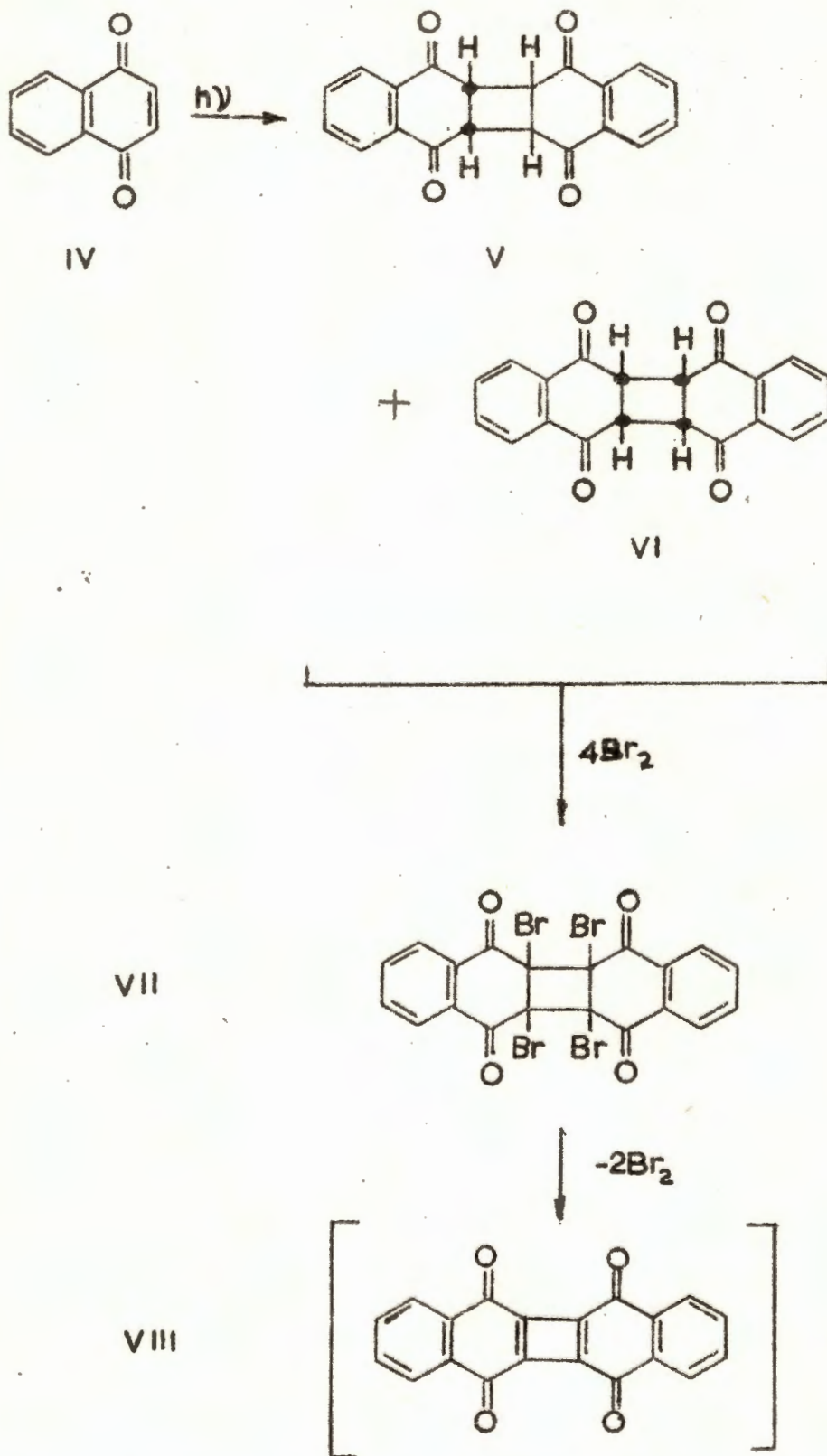


III

It can be assumed that the incorporation of additional stabilizing factors are essential for a cyclobutadiene to exist in an uncomplexed form. The four carbonyl groups, adjacent to the cyclobutadiene ring in hypothetical structure VIII, should have such a stabilizing influence. In order to obtain VIII it is necessary to synthesize and characterize a tetrahalogenated derivative of the C₄-dimer of 1, 4-naphthoquinone (IV).

The photolytic dimerization of 1, 4-naphthoquinone (IV) was first reported by Schönberg and Mustafa.⁴⁾ It was recently established that the dimer formed (V) has an anti configuration.⁵⁾ The transformation of IV to the isomeric syn dimer (VI) can also be done in the solid state.⁵⁾ Since both the anti (V) and syn (VI) dimers contain four tertiary hydrogen atoms, bonded to the cyclobutane ring and in an alpha position with respect to the four carbonyl groups, enolization should take place in both isomers. Bromination should therefore be possible, and, in an attempt to prepare the tetrabrominated derivatives of V and VI the same compound, with composition C₂₀H₈O₄Br₄, was obtained in both cases.^{6,7)}

(ii)



The aim of this study was to gain a better understanding of the chemistry of VII and to determine by means of X-ray diffraction methods the molecular structure and stereo-chemistry of VII.

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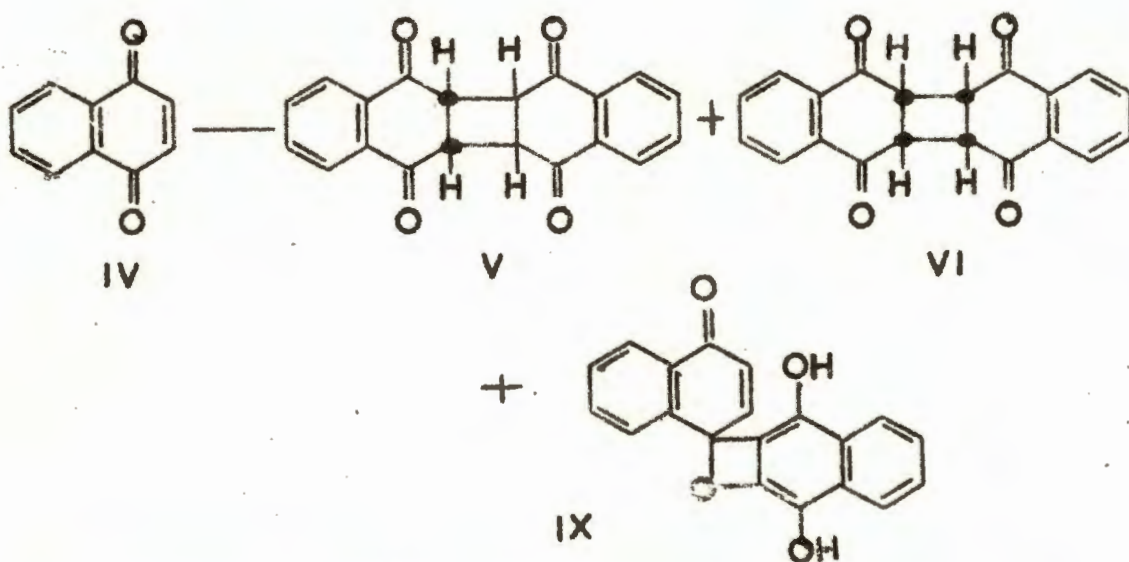
CHAPTER 1

THE BROMINATION OF THE ANTI (V) AND SYN (VI)

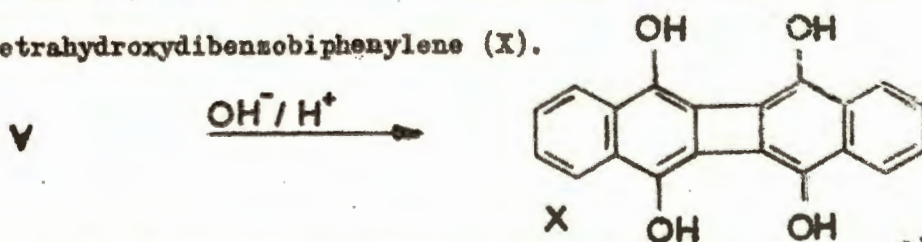
DIMERS OF 1, 4-NAPHTHOQUINONE (IV)

1.1 The Chemistry of the photodimers of 1, 4-naphthoquinone (IV)

During a reinvestigation⁵⁾ of the photolysis of 1, 4-naphthoquinone (IV) done recently, it was found that of the three different dimers which are formed, the anti dimer (V) is predominant. The syn dimer VI could be obtained by another method as well, i.e. the sunlight-irradiation of IV in the solid state.⁵⁾ Preliminary investigation⁷⁾ showed that the third dimer is of the oxetane type (IX).



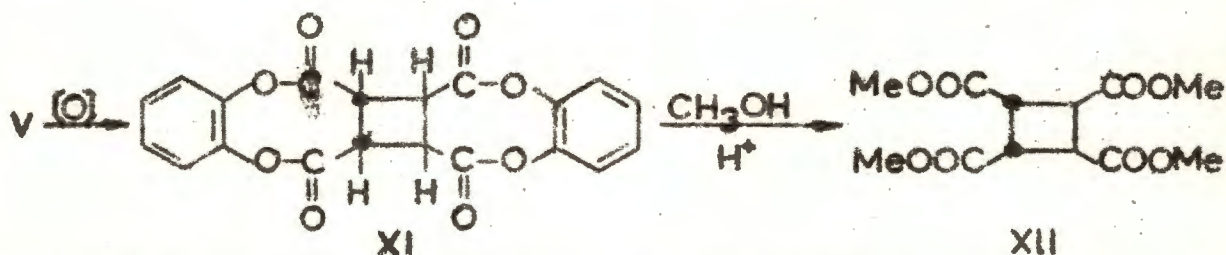
According to Bruce⁸⁾ V enolizes fairly easily in alkaline media, producing tetrahydroxydibenzobiphenylene (X).



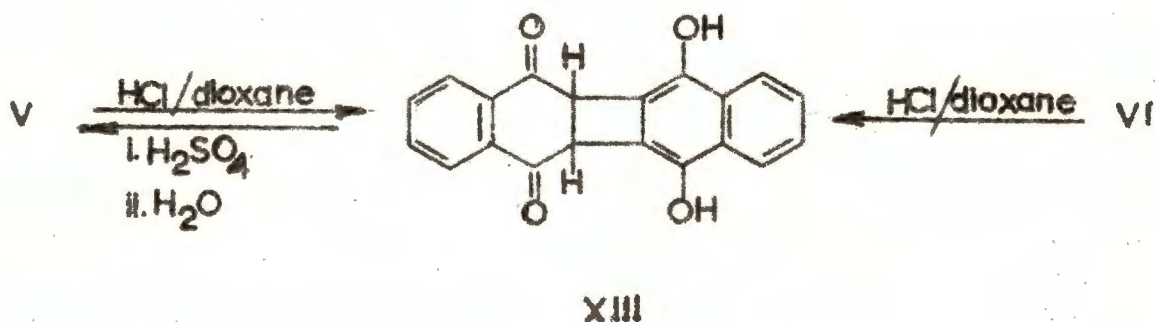
On the basis of simplified calculation, Coulson and coworkers⁹⁾ suggested that the four inner π -bonds of dibenzobiphenylene are highly localised. Keeping this in mind, Dekker and coworkers⁵⁾ succeeded in ketonizing X to V. These results borne out the argument that V has an anti-configuration. In addition it was shown⁵⁾ that the isomerization of

/the

the highly strained syn dimer (VI) to V can be accomplished quantitatively in acidic media. Unambiguous proof of the correctness of the configuration of V was finally obtained⁵⁾ by a Bayer-Villiger oxidation of V to the tetralactone XI, which was transformed to the tetramethyl ester (XII) of cis-trans-cis-cyclobutane-tetracarboxylic acid.



Both V and VI can be converted to the diketodihydroxy isomer XIII in dioxane containing hydrochloric acid.¹⁰⁾ The conversion of XIII to the anti dimer (V) was accomplished by dissolving XIII in concentrated sulphuric acid and adding this solution to excess water.¹⁰⁾

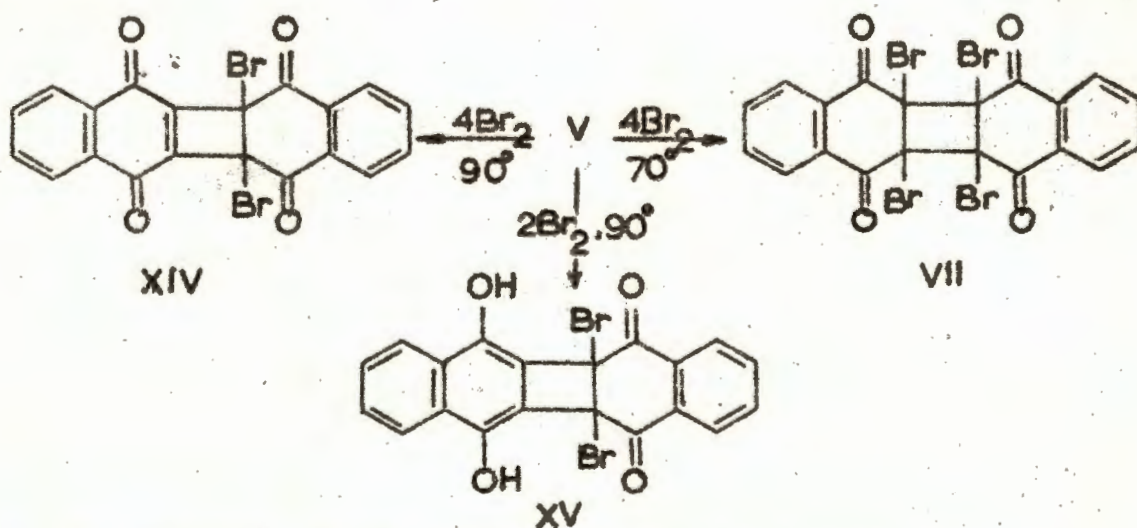


1.2 The bromination of the anti dimer (V)

In a series of experiments⁶⁾ it was established that the nature of the bromination products obtained when V was treated with bromine in acetic acid under different conditions, is highly temperature dependent. A tetrabromo derivative with composition $C_{20}H_8O_4Br_4$ was obtained when V was treated with four moles bromine at 70° . On the basis of its infrared⁶⁾ and mass⁷⁾ spectra the most probable structure is structure VII. The big similarity in the infrared spectra of the anti dimer (V) and the tetrabrominated derivative (VII) led to the belief that VII probably exists in the anti configuration.

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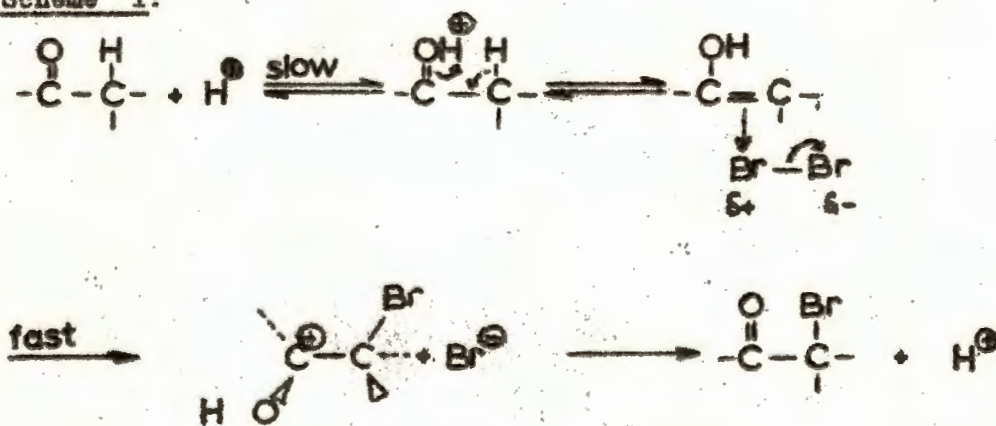
When the bromination was carried out at 90° , a dibromo derivative $C_{20}H_{10}O_4Br_2$ ⁶⁾ was formed. The infrared spectrum indicated the presence of an olefinic unsaturation (1630 cm^{-1}), suggesting that this dibromide should have structure XIV. A second dibromo derivative of V, $C_{20}H_{10}O_4Br_2$, could be obtained⁶⁾ by treating V with two moles bromine at 90° . A strong hydroxylic absorption at $3000 - 3450\text{ cm}^{-1}$ and the presence of two relatively strong bands (1635 and 1605 cm^{-1}) in the region associated with $C = O$ stretching vibrations, indicated⁷⁾ that this dibromide most probably possesses structure XV.



1.3 The structural relationship between the tetrabromide (VII) and the dibromides (XIV) and (XV)

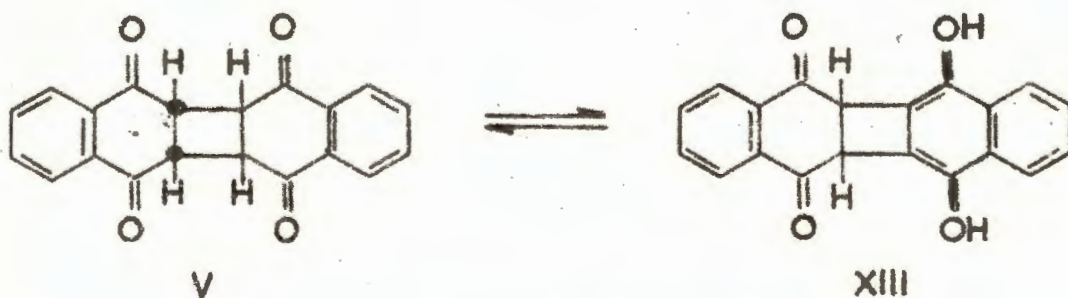
Lapworth¹¹⁾ has shown that the rate-controlling step in the acid-catalysed bromination of a ketone is the formation of the intermediate enol form of the substrate. The primarily formed enolic intermediate exerts a nucleophilic attack on bromine:

Scheme I:



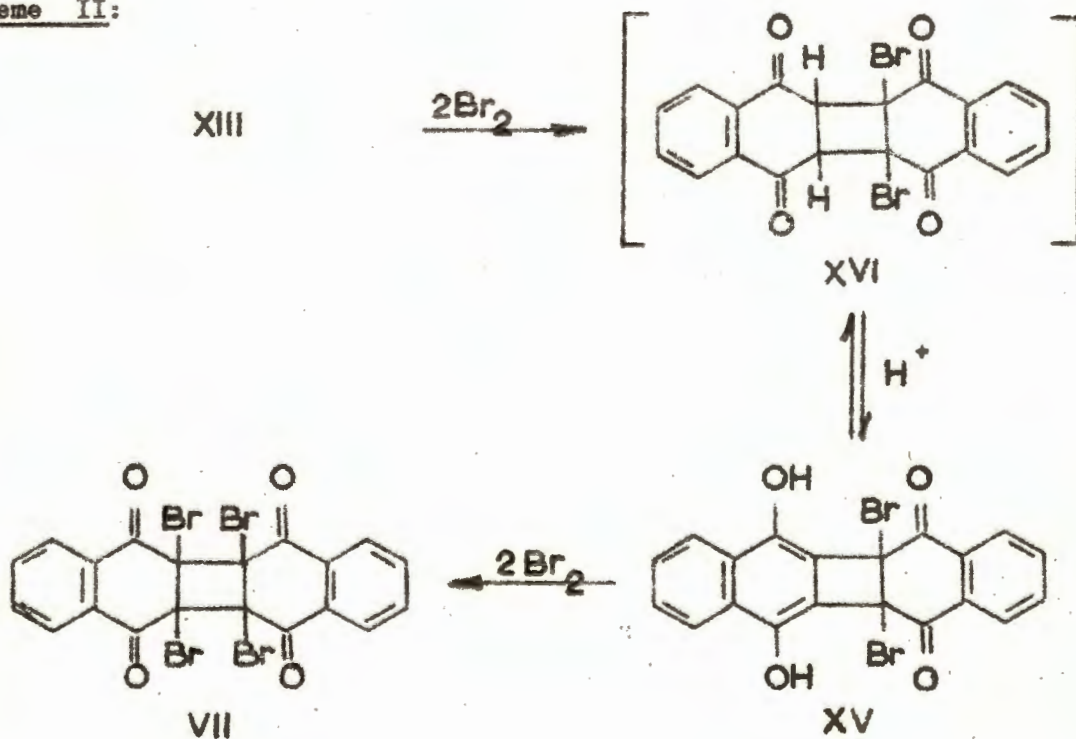
Venter found⁷⁾ that both the anti (V) and syn (VI) dimers of 1, 4-naphthoquinone lead to the same tetrabromo derivative (VII). His suggestion that the bromination proceeds, in both cases, via tetrahydroxy-dibenzo-biphenylene (X), seems doubtful since it has recently been established¹⁰⁾ that X ketonizes fairly rapidly in hydroxylic solvents such as ethanol, to both V and VI.

One may thus assume that the following equilibrium exists when V is dissolved in acetic acid:



Electrophilic attack of two moles bromine on XIII would result in the formation of a hypothetical dibromide (XVI), which should enolize to the dibromide (XV). If the conditions are favourable, XV would, on reaction with two more moles bromine lead to the tetrabromo derivative (VII).

Scheme II:



Evidence of the correctness of structure XV as well as the suggested reaction path, was obtained by treating a solution of XV in methylene chloride with excess bromine at room temperature, whereupon a colourless product, identical to VII, precipitated

Since the bromination of V with excess bromine at 90° , should take place according to Scheme II, the tetrabromide (VII) should be an intermediate in the formation of the olefinic dibromide (XIV). The transformation from "intermediate" VII to the dibromide (XIV) can be explained as a thermal elimination of bromine, which is not an unusual phenomenon,¹²⁾ especially when two cis-orientated bromine atoms have a steric influence upon each other. On refluxing VII in acetic acid, the solution gradually darkened in colour. Evaporation of the solvent led to the isolation of yellow crystals, of which the melting point and the infrared spectrum was identical to that of the dibromide (XIV). The reverse of this dehalogenation, i.e. the bromination of XIV to the tetrabromide (VII), was accomplished by ultra-violet irradiation of a solution of XIV in methylene chloride, in the presence of excess bromine. The colourless product was shown to be identical with VII.

1.4 Experimental

The photolysis of 1, 4-naphthoquinone (IV).

A solution of IV (1 g.) in acetic anhydride (12.5 ml) was sealed in a Pyrex test tube, and irradiated with a medium pressure U.V. lamp at room temperature for two weeks. The off-white precipitate (V, 0.2 g) crystallised from glacial acetic acid in colourless plates, melting with decomposition at $246 - 8^{\circ}$ (Lit:⁴⁾ $244 - 8^{\circ}$).

The bromination of V with four moles bromine at 70°

A solution of V (0.1 g) in acetic acid (40 ml) was heated to 90° . Immediately after addition of bromine (0.233 g) the temperature was lowered to 70° . The magnetically stirred solution decolourised within twenty

/minutes

minutes. The stirring was discontinued and the reaction mixture allowed to cool down slowly. Colourless crystals (VII, 0.18 g) separated, melting with decomposition at $255 - 8^{\circ}$ (Lit:⁶) $255 - 8^{\circ}$).

The bromination of V with four moles bromine at 90°

A solution of V (0.1 g) in acetic acid (40 ml) was treated with bromine (0.233 g) at 90° . The temperature was maintained at 90° and the reaction mixture treated as above. The yellow needles (XIV, 0.065 g) melted with decomposition at $276 - 8^{\circ}$ (Lit:⁶) $276 - 8^{\circ}$).

The bromination of V with two moles bromine at 90°

A solution of V (0.1 g) in acetic acid (40 ml) was treated with bromine (0.1045 g) at 90° as above. The yellow needles (XV, 0.054 g) melted with decomposition at $192 - 4^{\circ}$ (Lit:⁶) $192 - 4^{\circ}$).

The thermal dehalogenation of the tetrabromide (VII)

A mixture of VII (0.1 g) and acetic acid (50 ml) was refluxed for two hours. The clear solution was concentrated to 20 ml and cooled down to room temperature. The yellow crystalline product (XIV, 0.02 g) was identical to an authentic sample of XIV.

The bromination of the dibromide (XIV)

A solution of XIV (0.05 g) in methylene chloride (25 ml) containing bromine (0.030 g) was irradiated for ten minutes by means of a medium pressure U.V. lamp at room temperature. The tetrabromide (VII, 0.047 g) was obtained on concentration of the solution.

The bromination of the dibromide (XV)

A solution of XV (0.05 g) in methylene chloride (25 ml) containing bromine (0.05 g) was magnetically stirred for one hour. The tetrabromide (VII, 0.039 g) was isolated on concentration of the solution.

CHAPTER 2

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRABROMINATED
PHOTODIMER OF 1, 4-NAPHTHOQUINONE

2.1 Experimental

Most of the techniques used in this analysis are standard crystallographic practices and are described in various textbooks on the subject.^{13,14,15)}

The tetrabromide (VII) crystallized out as small crystals with an oblique rhombic habit. The β -angle was well defined and all three faces were developed to the same extent. The unit cell dimensions were determined from oscillation photographs about \underline{b} and \underline{c} , and from (hk0) and (h0 ℓ) equi-inclination Weissenberg photographs.

The crystal belongs to the monoclinic system with cell parameters:

$$a = 11.64 \pm 0.05 \text{ \AA}$$

$$b = 12.70 \pm 0.05 \text{ \AA}$$

$$c = 14.25 \pm 0.05 \text{ \AA}$$

$$\beta = 116^\circ \pm 1^\circ$$

The conditions for possible reflections were found to be: hk ℓ for $h + k = 2n$, h0 ℓ for $\ell = 2n$, which defines the space group C2/c, or its non-centrosymmetric counterpart Cc. The latter was ruled out by the successful structure analysis using C2/c.

The density was measured by flotation as 2.187 gm cm^{-3} . This agrees fairly well with the density of 2.22 gm cm^{-3} calculated for four molecules per unit cell.

Two different crystals were used for the data collection; the one mounted along \underline{b} , the other mounted along \underline{c} . Three-dimensional intensity data were collected on equi-inclination Weissenberg photographs by using the multiple film technique (see appendix A). Nickel-filtered CuK_α radiation were used and three layer lines in the (h0 ℓ) zone and eight layer lines in the (hk0) zone were recorded. Measurement of intensities was

/ done

done by visual comparison of the spots on the films with a series of standard spots on a calibrated wedge and unobserved reflections were given a value of $1/3 I_{\min}^{16)}$ All the intensities were corrected for Lorentz, polarisation and spotshape factors, making use of the computer program CORRECT, written by E.G. Boonstra for use on the IBM 360/40 (see appendix B). No correction was made for absorption as two different crystals with different sizes were used and the one crystal was mounted in such a way as to invalidate a cylindrical approximation for absorption corrections.

The values of kI_{corr} ($k = \text{scale factor}$) for the reflections on different layer lines, were scaled internally by comparing the magnitudes of the various sets of reflections having the same indices and which were recorded in both zones. A total of 1397 reflections was obtained, with 372 unobserved.

2.2 Structure determination and refinement

A crystal structure will be completely solved if the electron density function, $\rho(x,y,z)$, throughout the whole cell can be evaluated. From the theory of X-ray diffraction and Fourier transforms, it can be shown that the electron density distribution at every point in a crystal may be expressed as a Fourier series

$$\rho(x,y,z) = \sum_h \sum_k \sum_l \frac{F(hkl)}{V} e^{-2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)}$$

where $\rho(x,y,z) = \text{electron density at the point } (x,y,z)$

$(x,y,z) = \text{fractional coordinates of a point w.r.t. the unit cell origin and axes}$

$F(hkl) = \text{structure factor of the reflection } (hkl)$.

It is convenient to write this Fourier Series in the form

$$\rho(xyz) = \sum_{- \infty}^{\infty} \sum_{- \infty}^{\infty} \sum_{- \infty}^{\infty} \frac{|F(hkl)|}{V} \text{Cos} \left[\frac{2\pi hx}{a} + \frac{2\pi ky}{b} + \frac{2\pi lz}{c} - \alpha(hkl) \right]$$

where $\alpha(hkl)$ represents the phase constant associated with the amplitude

Although the observed intensities enables one to calculate $|F(hk_l)|$, no information is provided concerning the relative values of the phase constants. This so-called phase problem can be overcome by various methods, the most convenient being the Patterson synthesis to find the positions of the heavy atoms, which are then used to phase the structure factors.

The Patterson Synthesis

The Patterson function $P(uvw)$, which may be called the weighted average distribution of density of scattering matter about a point (xyz) in the crystal, is defined as

$$P(uvw) = \frac{1}{V} \int_0^a \int_0^b \int_0^c \rho(xyz) \rho(z+u, y+v, z+w) dx dy dz.$$

In this expression, if $(x+u, y+v, z+w)$ gives the distribution about (xyz) as a function of the parameters u, v, w , and it represents a distribution similar to $\rho(xyz)$ but displaced from the point (xyz) through a distance whose components are (u, v, w) . By expanding the two density functions as Fourier series and integrating, the Patterson function reduces to

$$P(uvw) = \frac{1}{V^2} \sum_h \sum_k \sum_l F^2(hk_l) e^{-2\pi i (\frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c})}$$

The function can thus be calculated in terms of the squares of the structure factors, that is, the observed intensities.

The function $P(uvw)$ is of great value in crystal analysis because it can only attain a large value when both $\rho(xyz)$ and $\rho(x+u, y+v, z+w)$ have large values. This will occur when there are atoms situated at both (x, y, z) and $(x+u, y+v, z+w)$, separated by the vector distance (uvw) . Thus a maximum in the function $P(uvw)$ at (u_1, v_1, w_1) corresponds to an interatomic distance in the crystal defined by a vector whose components are u_1, v_1, w_1 . The final summation of this function can therefore be interpreted as a three-dimensional interatomic vector map in which the maxima / define

define vectors from the origin. Because the peak heights are roughly proportional to the products of the atomic numbers of the atoms concerned, the vectors between heavy atoms can usually be easily distinguished. The Fourier coefficients of the Patterson Synthesis are all real, so that it will always possess a centre of symmetry. This means that the symmetry of the Patterson function is equal to or higher than that of the electron density.

The interpretation of a Patterson synthesis can be carried out by isolating the interatomic vectors between symmetry-related atoms, called the Harker vectors. In the case of the space group $C2/c$, the symmetry-related atoms in general positions are situated at

x, y, z	$\frac{1}{2} + x, \frac{1}{2} + y, z$
$\bar{x}, \bar{y}, \bar{z}$	$\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$
$x, y, \frac{1}{2} - z$	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
$x, \bar{y}, \frac{1}{2} + z$	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z.$

The Harker peaks corresponding to the vectors between them will then be found at the following values of (u,v,w) :

$0, 0, 0$	$\frac{1}{2}, \frac{1}{2}, 0$
$2x, 2y, 2z$	$\frac{1}{2} - 2x, \frac{1}{2} - 2y, - 2z$
$-2x, 0, \frac{1}{2} - 2z$	$\frac{1}{2} - 2x, \frac{1}{2}, \frac{1}{2} - 2z$
$0, 2y, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2} - 2y, \frac{1}{2}$

All the intensities measured were used for the calculation of a three-dimensional Patterson Synthesis by means of the centrosymmetric Fourier program written by Gantzel and Hope (U.C.L.A.) and modified for use on the 360/40 by Miss J. Hewitt. The function $P(u,v,w)$ had in this case space group symmetry $C2/m$, and it was therefore only calculated for the region $0 \leq u \leq \frac{1}{2}, 0 \leq v \leq \frac{1}{2}, 0 \leq w \leq \frac{1}{2}$.

With 16 bromine atoms in the unit cell, two sets of Harker peaks must be formed, with the two atoms in the asymmetric unit in positions (x_1, y_1, z_1) and (x_2, y_2, z_2) . By comparing the strongest peaks along the

/edge

edge $w = \frac{1}{2}$ of the plane $u = 0$, the vectors $(0, 2y, \frac{1}{2})$ could be found. With the y -coordinates of the bromine positions known, the x and z -coordinates were easily found. Their correctness were checked by calculating the direct vectors between the positions (x_1, y_1, z) and (x_2, y_2, z_2) and comparing these vectors with the peaks formed at the corresponding (u, v, w) .

Two possible solutions remained:

$$(x_1, y_1, z_1) = (0.075, \mp 0.095, 0.125)$$

$$(x_2, y_2, z_2) = (0.175, \mp 0.150, 0.230)$$

Because they are equivalent, there could not be distinguished between them.

The coordinates of the heavy atoms in the trial structure were chosen as

$$x = 0.075, y = 0.095, z = 0.125$$

$$\text{and } x = 0.175, y = -0.150, z = 0.230.$$

The Fourier Synthesis

As shown above, the electron density distribution in the crystal may be written as

$$\rho(xyz) = \sum_h \sum_k \sum_l \frac{|F(hkl)|}{V} \cos \left[\frac{2\pi hx}{a} + \frac{2\pi ky}{b} + \frac{2\pi lz}{c} - \alpha(hkl) \right]$$

In the centrosymmetrical case the phase angle $\alpha(hkl)$ is restricted to 0 or π , so that

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l \pm F(hkl) \cos 2\pi \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right).$$

When the position of a heavy atom is known, and included in this summation, its contribution to the average structure factor amplitude will dominate that of the light atoms so that the phase will be approximated. From successive approximations by the Fourier method, with the heavy atoms in the trial structure, the positions of the other atoms can be found.

Unfortunately, because the major portion of the structure amplitude is due to the heavy atom contribution, all information concerning the light atoms must be derived from the smaller remaining part of the structure amplitude.

Thus the accuracy of their determination is reduced. The presence of the heavy atom also means a higher absorption coefficient and makes the correction of intensities more difficult.

The square roots of the intensities that were used for the Patterson Synthesis were used for the calculation of the Fourier Synthesis phased by the contribution of the bromine atoms. Again the centrosymmetric Fourier program by Gantzel and Hope was used for the computation. This three-dimensional electron density distribution map immediately yielded all the other atomic positions.

Refinement

The refinement of the trial structure was done on the IBM 360/40 computer of the CSIR, using the full-matrix least-squares program ORFLS of Busing, Martin and Levy and atomic scattering factors as supplied by Hanson et al.¹⁷⁾ (Alterations to ORFLS as well as the function and error program ORFFE to allow their use on the 360/40 were made by H. Messerschmidt of IBM (S.A.)).

The theory of least-squares refinement is well-known and described in various texts.^{4,5)} Basically this method changes the atomic coordinates of the trial structures in such a way as to improve the agreement between the observed structure factors (F_o) and the structure factor values calculated from the trial structure (F_c). The quantity minimized by the program ORFLS is $\sum w (F_o - k|F_c|)^2$, where w is the weight of a particular term and is usually taken as inversely proportional to the square of the standard error in $|F_o|$. The program refines the scale factors, positional atomic parameters, the overall temperature factor, isotropic or anisotropic individual temperature factors as required.

The overall agreement between the observed and calculated structure factors is expressed in terms of the mean discrepancy

$$R = \frac{\sum_{hkl} (|F_o| - |F_c|)}{\sum |F_o|}$$

R is called the residual or reliability factor and is usually expressed as a percentage.

Using all the observed intensities, the scale factor, the overall temperature factor, the atomic coordinates and the isotropic individual temperature factors were refined. The value of R at this stage was 16.4%. A refinement of the anisotropic thermal coordinates was attempted but it yielded a non-positive definite tensor for carbon (2) (see figure 1). Up to this stage of the refinement no differential weighting was applied and w was given a value of 1 for all reflections. Various weighting schemes were now applied but none of them improved the value of R. This could be a result of absorption effects for which no corrections were applied to the measured intensities. The conformation of the molecule was, however, established beyond any doubt at this stage and the refinement of the isotropic thermal parameters was taken to completion. Refinement was considered complete when all parameter shifts were less than one tenth of their estimated standard deviations. The value of R remained at 16.3%.

The final atomic parameters and their estimated standard deviations are given in Table I (see figure 1). The observed and calculated structure factors on an absolute ($F_{000} = 1168$) scale are compared in Table II.

Interatomic approaches and bond angles were calculated by means of the function and error program ORFFE of Busing, Martin and Levy.

2.3 Discussion of the structure

Two projections of the symmetry elements of the space group C2/c are shown in figure 2 and the same projections of the unit cell contents are shown in figure 3. Comparison of the two figures clearly shows that a crystallographic two-fold axis coincides with a molecular two-fold axis. The molecule is, however, distorted away from the regular centrosymmetrical anti configuration. All bond lengths and angles are shown in figure 4, and all meaningful intramolecular distances between non-bonded atoms are tabulated in Table II. All intermolecular approaches were found to have the normal

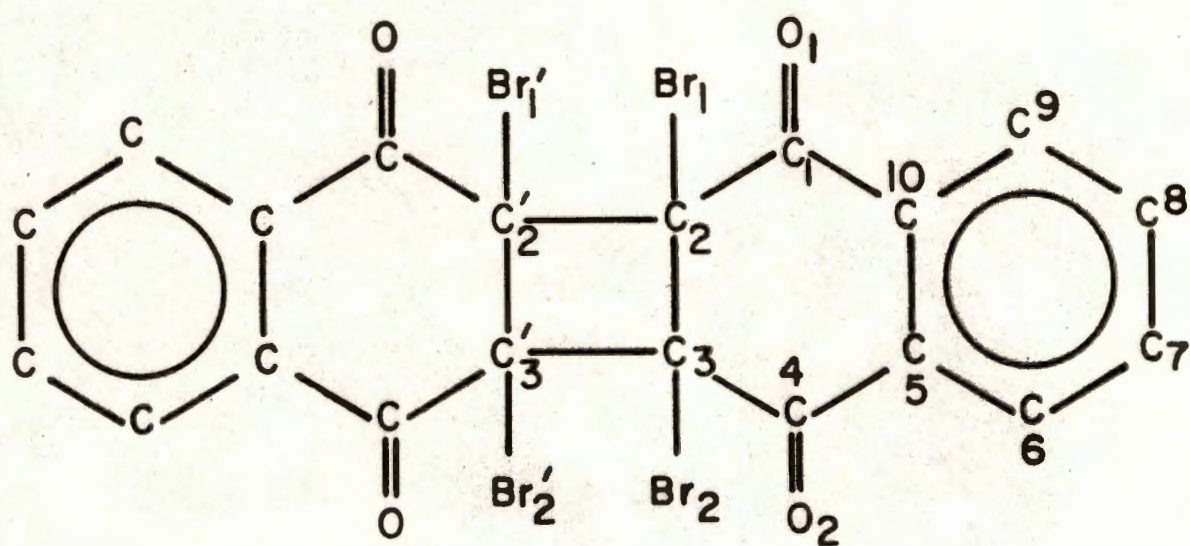


Fig. 1. Structural formula of tetrabromide (VII) (excluding hydrogen atoms) showing the nomenclature used in this analysis.

Atom	x	y	z	B(\AA^2)
Br(1)	0.5711 0.0002	0.5936 0.0002	0.1241 0.0002	3.13 0.06
Br(2)	0.6713 0.0002	0.3527 0.0002	0.2267 0.0002	3.52 0.06
O(1)	0.6621 0.0016	0.7254 0.0014	0.3234 0.0015	3.79 0.35
C(2)	0.6123 0.0018	0.3349 0.0016	0.4287 0.0016	4.66 0.41
C(1)	0.6690 0.0020	0.6327 0.0018	0.3397 0.0019	2.62 0.40
C(2)	0.5702 0.0015	0.5617 0.0014	0.2600 0.0015	1.38 0.29
C(3)	0.5743 0.0020	0.4409 0.0018	0.2764 0.0020	2.91 0.43
C(4)	0.6414 0.0022	0.4135 0.0019	0.3944 0.0020	3.23 0.45
C(5)	0.7529 0.0021	0.4794 0.0019	0.4595 0.0020	3.00 0.43
C(6)	0.8431 0.0024	0.4365 0.0021	0.5499 0.0022	3.89 0.51
C(7)	0.9563 0.0028	0.4948 0.0024	0.6140 0.0025	4.71 0.61
C(8)	0.9637 0.0029	0.5942 0.0025	0.5886 0.0026	5.07 0.66
C(9)	0.8727 0.0025	0.8431 0.0022	0.5009 0.0023	3.92 0.52
C(10)	0.7658 0.0021	0.5794 0.0018	0.4327 0.0020	2.90 0.42

TABLE I: Fractional atomic coordinates and individual temperature factors and their estimated standard deviations

Van der Waal's magnitude, and are not listed. The estimated standard deviations averaged over similar types of bond are shown in Table IV.

As shown in figure 4, the lengths of chemically similar, but crystallographically distinct, bonds are nowhere significantly different. The regular variation of the bond lengths in the benzene ring could be meaningful, since the ring is somewhat distorted towards a boat form (see figure 5). The mean plane through the benzene ring is given by

$$0.7953 u + 0.3182 v - 0.5160 w = 3.759$$

where u , v and w are orthogonal coordinates (in Å units) related to the fractional coordinates x , y and z of the atoms in the monoclinic axial system by the equations

$$u = xa + 2c \cos \beta$$

$$v = yb$$

$$w = 2c \sin \beta.$$

The deviations of the atoms from this plane are shown in figure 4, and although they are not beyond experimental error they seem to indicate a localized double bond between C (5) and C (10) when considered in conjunction with the variation in bond lengths. This may be due to the presence of the quinoid system in the contiguous ring.

The most interesting and important structural feature of this molecule is the cyclobutane ring (see figures 4, 5 and 6). This ring is not flat but markedly distorted towards a tetrahedron, as shown in figure 5. The deviations from planarity refer to the mean plane

$$- 0.3066 u + 0.9519 w = 1.742$$

which also contains the crystallographic and molecular two-fold axis.

The bond lengths in the cyclobutane ring compare well with the corresponding bond lengths in 1, 2, 3, 4-tetraphenylcyclobutane. This structure was determined by Dunitz¹⁹⁾ and is also discussed in detail by Kitaigorodskii²⁰⁾.

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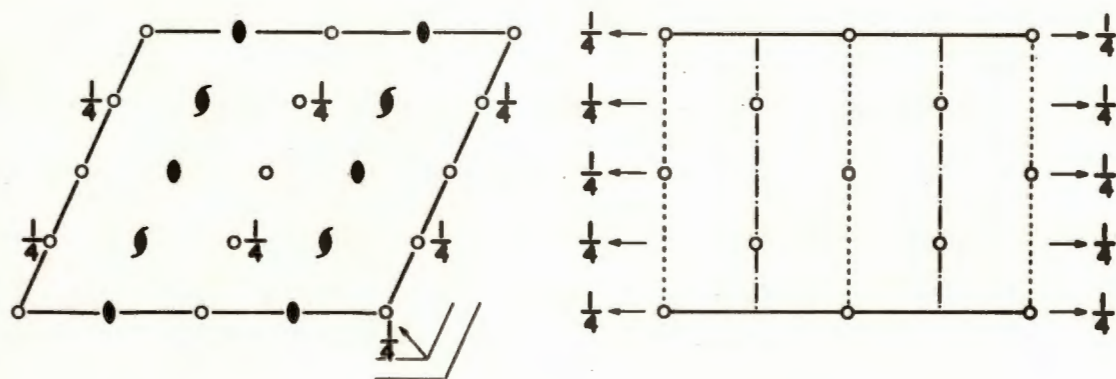


Fig. 2. (010) and (001) projections of the symmetry elements in space group $C2/c$.¹⁸⁾

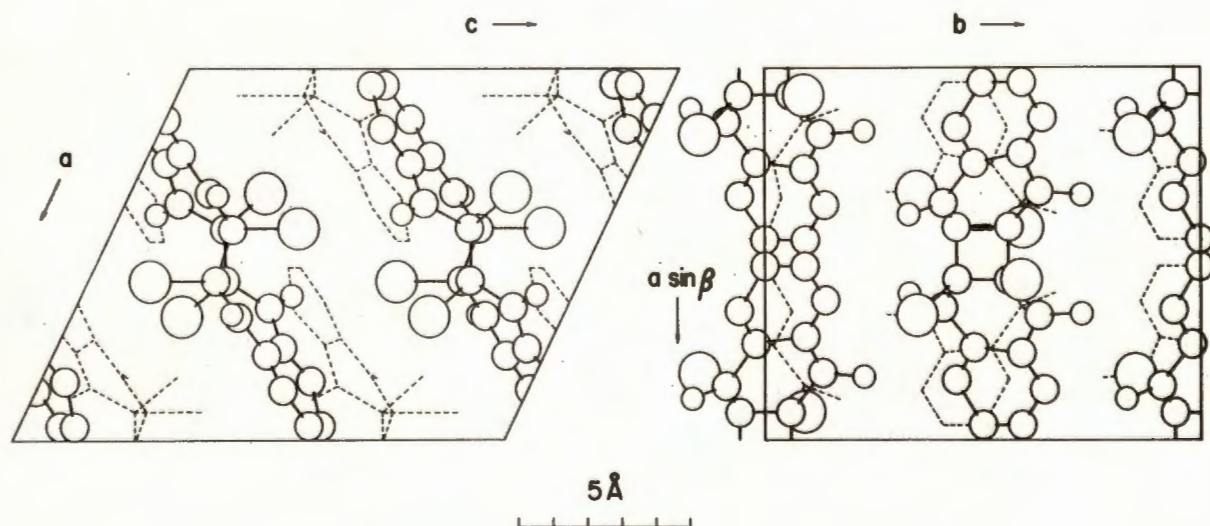


Fig. 3. (010 and (001) projections of the unit cell contents.

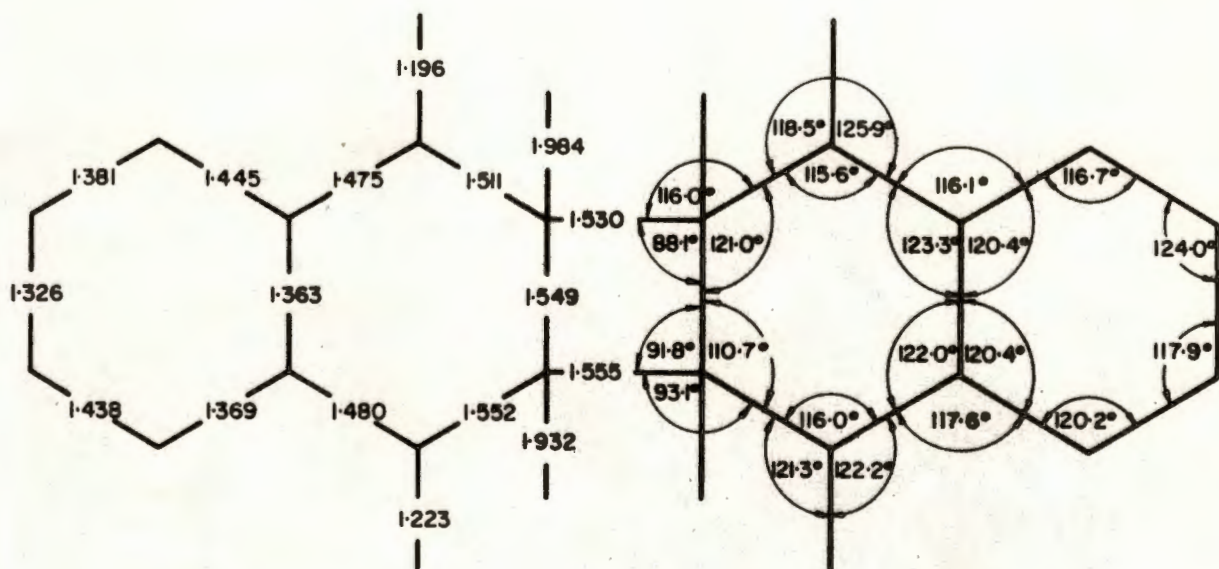


Fig. 4. Bond lengths and angles for the asymmetrical half of the molecule.

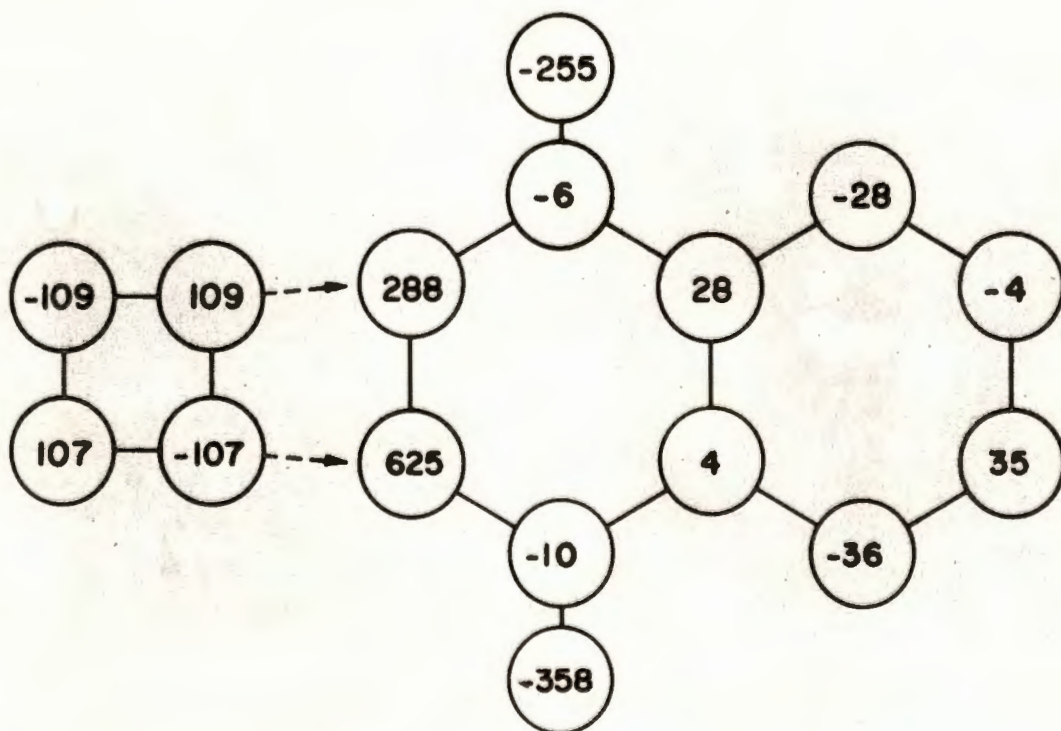


Fig. 5. Displacements (in $\text{Å} \times 10^3$) of the atoms from the mean plane through the cyclobutane ring (left) and from the plane through the benzene ring (right).

Contact	\AA
Br(1) ... Br(2)	3.370 \pm .004
Br(2) ... Br(2')	4.321 \pm .005
Br(1) ... Br(1')	4.563 \pm .005
Br(1) ... O(1)	3.058 \pm .019
Br(2) ... O(2)	3.248 \pm .021
Br(1) ... O(1')	3.538 \pm .023
Br(1) ... O(2')	3.809 \pm .024
Br(1) ... C(2')	2.824 \pm .019
Br(1) ... C(3)	2.898 \pm .025
Br(2) ... C(2)	3.024 \pm .018
Br(2) ... C(3')	3.053 \pm .023
Br(1) ... C(3')	3.277 \pm .024
Br(2) ... C(2')	3.930 \pm .021
O (1) ... O(1')	3.421 \pm .033
O (2) ... O(2')	4.594 \pm .041
O (1) ... C(2)	2.332 \pm .024
O (2) ... C(3)	2.425 \pm .032
C (2) ... C(3')	2.165 \pm .027

TABLE III: Intramolecular interatomic distances between non-bonded atoms.

Contact or angle	σ_m
(Br ... Br)	0.004 \AA
(O ... Br)	0.020 \AA
(C - Br)	0.022 \AA
(C - O)	0.028 \AA
(C - C)	0.035 \AA
(C $\overset{\wedge}{\text{C}}$ Br)	1.5 $^\circ$
(C $\overset{\wedge}{\text{C}}$ C)	2.0 $^\circ$
(O $\overset{\wedge}{\text{C}}$ C)	2.2 $^\circ$

TABLE IV: Mean values of the estimated standard deviations for various approached in the molecule.

The average value for the bond lengths found in the tetrabromide (IV) is 1.545 Å as compared to the average value of 1.570 Å obtained by Dunitz. The value found for the separation of diametrically opposed ring atoms is 2.165 Å compared to the Dunitz value of 2.2 Å.

The reason for the distortion in the structure lies in the positions of the four bromine atoms attached to the cyclobutane ring. For the ideal centrosymmetric structure, the bonds from a flat cyclobutane ring should be at half tetrahedral angles (54.5°) to its plane and their projections on the ring should lie at 45° to the diagonals, according to Kitaigorodskii.²⁰⁾ An error seems to have crept in, either in translation or in printing, since these projections should lie along the diagonals. Assuming the carbon-bromine bond length, $d(\text{C-Br})$, to be 1.937 Å,²¹⁾ and $d(\text{C-C})_{\text{cyclobutane}}$ to be 1.57 Å,²⁰⁾ the model which is explained in figure 7, gives

$$d(\text{Br-Br})_{\text{cis}} = d(\text{C-C}) + 2d(\text{C-Br}) \cos \varpi \sin \phi = 3.16 \text{ Å.}$$

This bromine-bromine separation is significantly less than twice the Van der Waal's radius of 1.9 Å for bromine.²²⁾ This overcrowding of the bromine atoms is relieved by the tetrahedral distortion of the cyclobutane ring. The parameters ϖ and ϕ which have the values 54.5° and 45° in the regular centrosymmetric structure, now have the values $\varpi_2 = 36^\circ$, $\phi_2 = 28^\circ$, $\varpi_3 = 59^\circ$, $\phi_3 = 36^\circ$ at C(2) and (3) respectively. The separation of the two bromine atoms in cis relationship is increased to 3.370 ± 0.004 Å by this distortion. Although significantly less than 3.8 Å this distance is comparable to the bromine-bromine separation in the overcrowded 1, 2; 4, 5-tetrabromobenzene,²³⁾ which is 3.377 ± 0.004 Å.

The carbon-oxygen bond length has an average value of $d(\text{C=O}) = 1.21$ Å, which fall within the normal range for double bonds between carbon and oxygen, of 1.18 to 1.23 Å.²⁴⁾

The main feature of the structure is thus the overcrowding of the bromine atoms in cis relationship which leads to distortion of the cyclobutane ring and is also reflected in the irregular shape of the quinoid ring.

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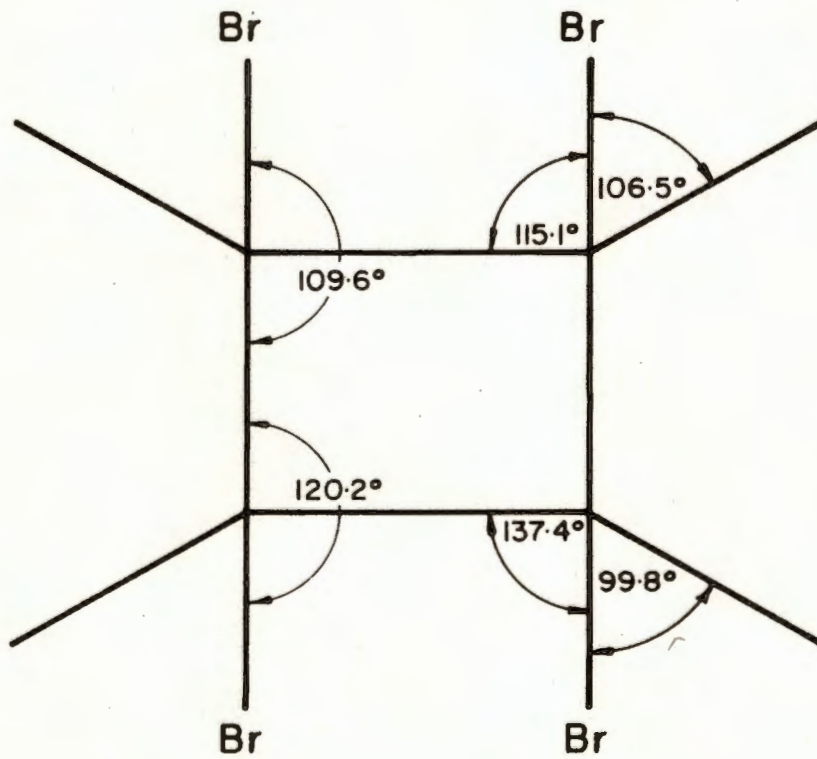


Fig. 6. Bond angles for the bonds between the cyclobutane ring and atoms bonded to it.

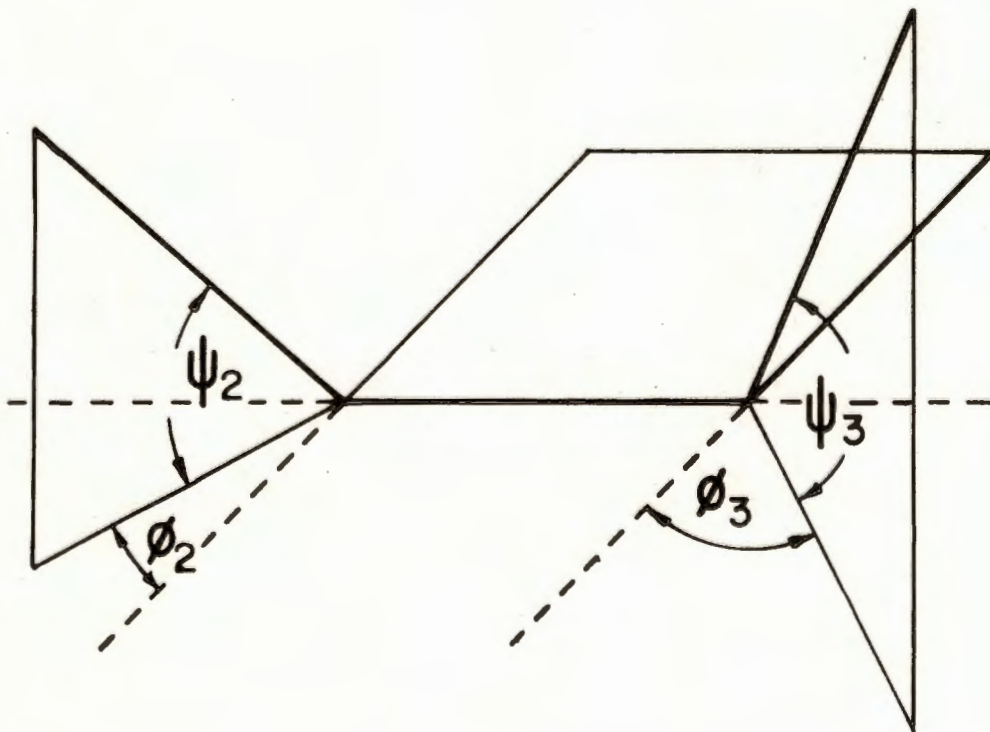


Fig. 7. The geometry of the cyclobutane ring and its connecting bonds using the model of Kitaigorodskii.²⁰⁾

The complete molecular conformation is shown in the perspective view in figure 8. It is interesting to note that this arrangement has been reached only by a distortion of the molecule, especially the cyclobutane ring, and does not involve a lengthening of the carbon-bromine bonds. Within experimental error they correspond in length with the mean $d(\text{C-Br})$ of $1.937 \pm 0.003 \text{ \AA}$ in polyhalogenated methanes.²⁵⁾ The lengthening of the central C - C bonds as predicted by Kitaigorodskii²⁰⁾ and Glocker²⁵⁾ is also not observed and apart from its non-planarity the cyclobutane ring can be described as a normal single-bonded four-membered ring.

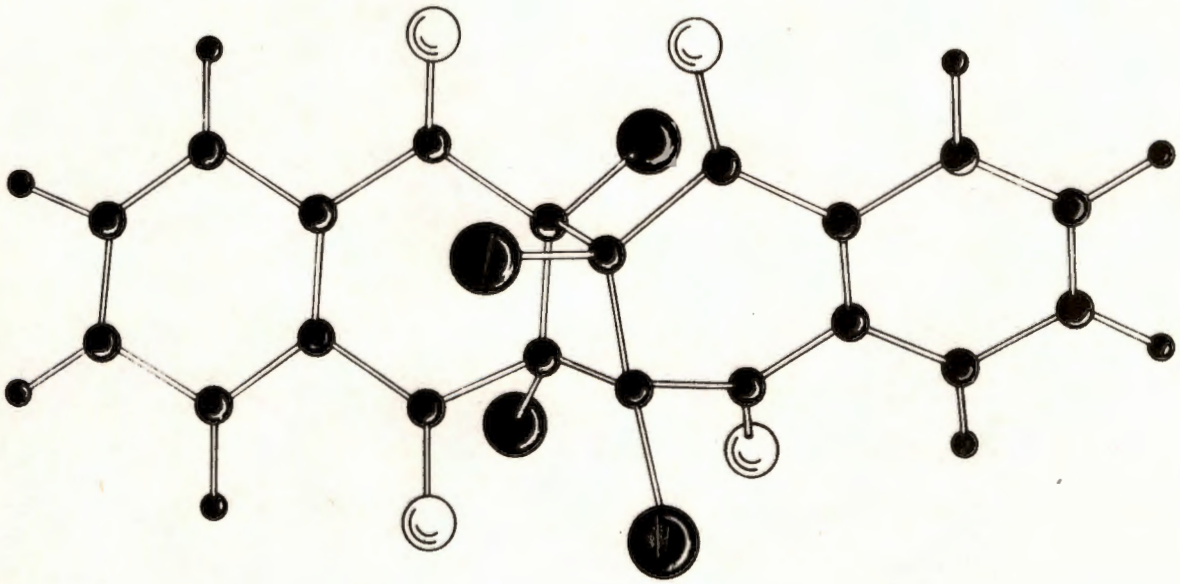


Fig. 8. Perspective view of the molecule to illustrate its conformation.

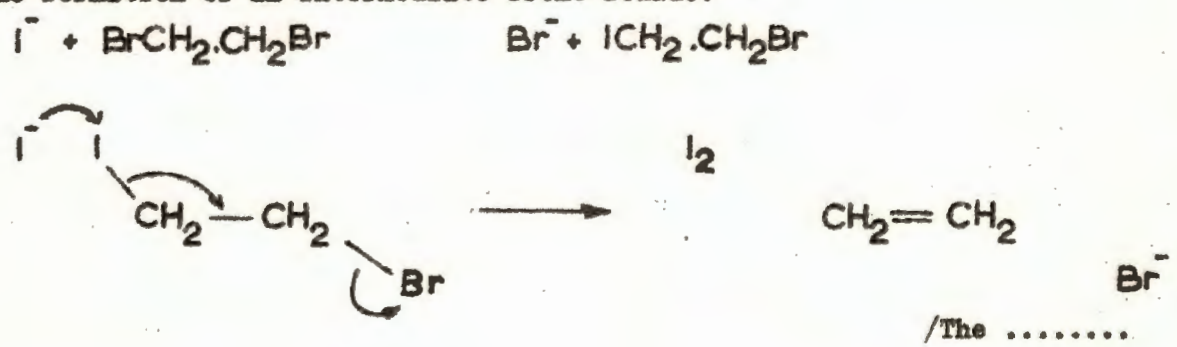
2.4 CONCLUSION

When the structure of the tetrabromide (VII) is examined closely the chemical significance of the configuration of the bromine atoms can be recognised. The overcrowding of the bromine atoms creates a strained molecule and this strain could be relieved by elimination of bromine. The successful thermal dehalogenation of VII to the dibromide (XIV) proves this expected reactivity. The stability against further thermal dehalogenation of XIV shows that the easy removal of bromine is related to the overcrowding.

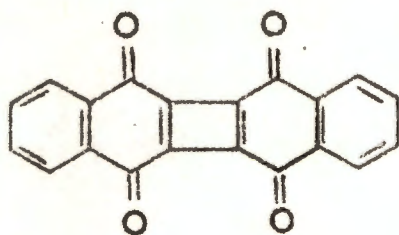
With the structure of the tetrabromide (VII) known, a possible mechanism for the synthesis of the suggested cyclobutadiene (VIII) by complete removal of the bromine, can be proposed. It has been shown that the higher reactivity of the strained molecule (VII) should make dehalogenation fairly easy. Furthermore, debromination of 1, 2-dibromides with zinc powder or iodide ion is well known.^{26,27)} The elimination by means of zinc normally proceeds stereospecifically trans as in the case of the debromination of three-2,3-dibromobutane to cis-2-butene:²⁶⁾



A similar stereospecificity is observed in the debromination by means of iodide ion. There is reason to believe that here the mechanism involves the formation of an intermediate bromo-iodide:²⁷⁾



The tetrabromide (VII) contains two pairs of trans orientated bromine atoms, so that the trans-elimination of bromine can be expected. Treatment of VII with debrominating agents such as zinc or iodide ion can thus result in the synthesis of the cyclobutadiene derivative (VIII):



S U M M A R Y

The chemical investigation of the relationship between the di- and tetrabrominated photodimers of 1, 4-naphthoquinone was undertaken and a mechanism for the bromination introduced. The crystal and molecular structure of the tetrabromide, $C_{20}H_8O_4Br_4$, was determined by three-dimensional X-ray diffraction methods. It was established that the molecule has the anti conformation in the solid state. It is considerably distorted because of overcrowding of the bromine atoms in cis relationship but the bond lengths are unaffected. The distortion is adequately described in terms of the non-planarity of the cyclobutane ring.

O P S O M M I N G

'n Chemiese ondersoek na die onderlinge verwantskap tussen die di- en tetragebromineerde fotodimere van 1, 4-naftakinoon is gedoen en 'n meganisme vir die bromeringsproses is voorgestel. Die kristal- en molekulêre struktuur van die tetragebromineerde derivaat, $C_{20}H_8O_4Br_4$, is met behulp van drie-dimensionele X-straaldiffraksiemetodes bepaal. Dit is vasgestel dat die molekule in die vaste toestand 'n anti konfigurasie het. Die molekule is aansienlik verwring as gevolg van die onderlinge afstoting tussen die broomatome in cis-verwantskap. Die bindingslengtes is egter nie verander nie. Die verbuiging word duidelik aangetoon deur die feit dat die siklobutaanring nie in 'n plat vlak lê nie.

A P P E N D I X A

INTENSITY MEASUREMENTS ON MULTIPLE FILMS.¹³⁾

With this method, a number of films, usually seven, are superimposed on each other in the camera, when recording the reflections. The intensity measurements from the different films of each layer line are placed on the same relative scale by applying factors to the measurements from each film. These interfilmfactors are obtained by taking the mean of the interfilm factors that can be calculated from the measured intensities for all the reflections. The intensity for each reflection is then given by the average of the values over all relevant films, after the filmfactors have been applied. A computer program, FILMFACT, was written by J. Admiraal and used to carry out this computation for each layer line.

With the multiple film method it is possible to obtain a set of uncorrected intensities over a much wider range than possible on a single photographic film.

A P P E N D I X B

CORRECTIONS TO MEASURED INTENSITIES

The corrections which have to be applied to the measured intensity (I_{meas}) of a reflection, to yield the corrected intensity (I_{corr}) and hence the observed structure factor (F_0), are standard for equi-inclination Weissenberg photographs. The relationship between I_{meas} and I_{corr} can be formulated as

$$I_{\text{corr}} = I_{\text{meas}} S \cdot C \cdot A^* \cdot S^* \cdot (Lp)^{-1}$$

- where
- S = scale factor applied to the intensities of each layer line to get F_0 on an absolute scale
 - C = splitting factor, as a result of splitting of spots due to the α_1, α_2 doublet of K radiation
 - A^* = absorption correction
 - S^* = spot shape factor for higher layer lines (Phillips, 1954)
 - Lp = combined Lorentz and polarization factor (Cochran, 1948).

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