rather short on the average. The obvious interpretation is that the conjugation is mostly directed round by way of these carbon atoms, giving a 20-atom conjugated ring: N(1)–C(1)–N(2)–C(8)–N(3)–C(9)–C(10)–C(11)–C(12)–C(13)–N(1′)– etc. Elvidge & Linstead (1952) suggested that this canonical form might contribute appreciably to the stabilization of III. The bond-lengths now reported support this suggestion, and amplify it by making it appear possible that this form is predominant.

I would like to thank Prof. J. M. Robertson, F.R.S., to whose interest and encouragement I was particularly indebted in carrying out this work.

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The Structures of Molecular Compounds Exhibiting Polarization Bonding. I. General Introduction and the Crystal Structure of Phenoquinone

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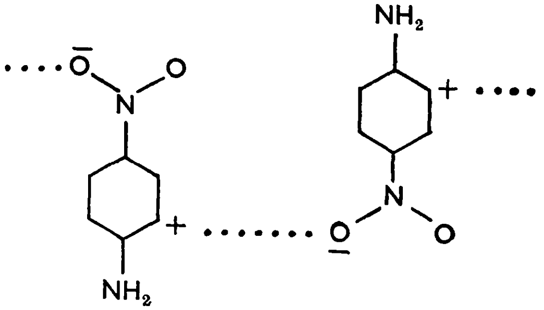
‘Polarization bonding’ is the term which has been introduced to describe the interaction between polarizing and polarizable molecules. In crystalline molecular compounds formed by nitro-compounds and quinones, such interaction is revealed by the unusual plane-to-plane stacking of the molecules rather than by a shortening of the van der Waals separations.

Crystals of phenoquinone, $(C_6H_5OH)_2.C_6H_4O_2$, are monoclinic, space group $P2_1/c$, with two formula units in each cell of dimensions $a_0 = 11{\cdot}16$, $b_0 = 5{\cdot}97$, $c_0 = 11{\cdot}48$ Å, $\beta = 100°$. By two-dimensional Fourier methods it is found that each quinone molecule is sandwiched between two centro-symmetrically related phenol molecules arranged parallel to the quinone with perpendicular separations of 3·33 Å. Such groups of three molecules are stacked in columns parallel to [201] and the columns are linked by hydrogen bonds of length 2·64 Å between phenolic OH groups and quinone oxygen atoms.

It is suggested that the polarization bonding in complexes of this type might be interpreted as the formation of partial molecular π-bonds.

Introduction: polarization bonding

The term ‘polarization bonding’ has recently been introduced (McKeown, Ubbelohde & Woodward, 1951) to describe the interaction between a polarizing molecule and a polarizable molecule, as found, for example, in molecular compounds formed by nitro compounds, quinones, etc. with aromatic hydrocarbons, amines and phenols. Although such bonding does not necessarily result in an unusually close approach of the two molecules, they regard the interaction between adjacent molecules in crystalline *p*-nitroaniline as being an extreme case of polarization bonding on the grounds of a close approach of 2·66 Å observed (Abrahams & Robertson, 1948) between an oxygen atom of the NO_2 group and the CH group *ortho* to the NH_2 group. A study of the thermal expansion of *p*-nitroaniline (McKeown *et al.*, 1951) reveals that the short intermolecular distance of the ‘polarization bond’ is associated with the direction of maximum coefficient of expansion and it is tentatively proposed that this may be accounted for by the overlap of two potential energy curves corresponding to resonance between the two structures



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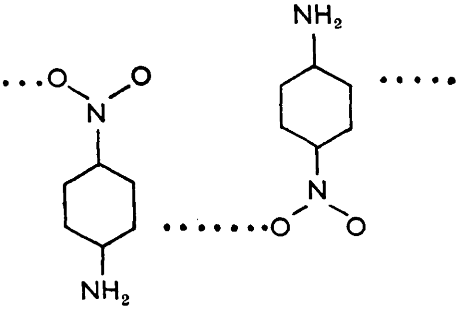


II

This scheme is suggested by the fact that the extrapolated value of the length of the polarization bond at absolute zero is consistent with reasonable values for the radii of the two adjacent ionic groups in structure I. This formulation of the polarization bond is somewhat similar to the electron transfer hypothesis put forward by Weiss (1942, 1943) to explain the bonding and the light absorption of the type of molecular compound mentioned above, except that Weiss regards the complete transfer of an electron as being the normal state, especially in the case of highly coloured complexes.

It has already been pointed out (Wallwork & Harding, 1953) that, in such series of molecular compounds as the quinhydrones and the complexes formed by trinitrobenzene with aromatic hydrocarbons and bases, the essential structural feature appears to be an unusual alternate plane-to-plane stacking of the molecules. This characteristic feature may be regarded as evidence for the existence of polarization bonds between the alternate polarizing and polarizable molecules. The nature of these polarization bonds and the extent of their effect on the packing of molecules is being investigated in this laboratory by the detailed crystal structure analysis of a number of molecular compounds.

A preliminary optical and X-ray study of quinhydrone suggested that the polarization bonding is responsible, not only for the structural arrangement, but also for the deep colour of the molecular compound. The marked pleochroism, in which the colour of thin crystals changes from deep blue to pale brown as the plane of incident polarized light is rotated, shows maximum light absorption when the electric vector is in a direction parallel to a column of alternate quinol and quinone molecules stacked plane to plane. This is in agreement with the observation (Tsuchida, Kobayashi & Nakamoto, 1951) that, in this type of structure, the maximum absorption is in a direction approximately perpendicular to the aromatic rings. In view of the report on the structure of quinhydrone presented by Nitta, Matsuda & Osaki to the International Union of Crystallography Congress at Stockholm in 1951, no detailed investigation of the structure of quinhydrone has been made in this laboratory. The preliminary study indicated, however, that pleochroism might be used as a rough test for this type of molecular compound and to provide an indication of the approximate orientation of the molecules.

Phenoquinone is an interesting member of the quinhydrone series in that it has the stoichiometric composition of two molecules of phenol to one molecule of benzoquinone. This is the composition to be expected if every OH group forms a hydrogen bond with a CO group, as in the 1:1 structure of quinhydrone. It is therefore to be expected that hydrogen bonding will play an important part in the structural arrangement as well as polarization bonding.

Preliminary investigation

Phenoquinone was obtained by mixing warm concentrated solutions of *p*-benzoquinone and phenol in petrol ether. The solutions, on mixing, gave a yellow colour and red lath-shaped crystals were deposited on cooling. When observed with plane polarized light the crystals appeared red when the electric vector was parallel to the long axis of the lath and yellow at right angles to this position. On exposure to the atmosphere for a few hours the crystals decomposed leaving a white skeleton, so the specimens used for X-ray photography were sealed into thin-walled pyrex capillary tubes immediately after preparation. Oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation showed that the crystal is monoclinic with

$$a_0 = 11{\cdot}16,\ b_0 = 5{\cdot}97,\ c_0 = 11{\cdot}48\ \text{Å},\ \beta = 100^\circ$$

and space group $P2_1/c$. The observed density of 1·278 g.cm.$^{-3}$ corresponds to two molecules of the complex $C_6H_4O_2.2C_6H_5OH$ in this cell, implying that the quinone molecules must be in special positions at centres of symmetry. They were chosen to be at the points 0, 0, 0 and 0, $\frac{1}{2}$, $\frac{1}{2}$. The intensities of reflexions on the Weissenberg photographs obtained by the multiple-film technique were measured by a method of direct photometry of the X-ray negatives (Wallwork & Standley, 1953) in which the transmission of each spot is compared with the transmission of an adjacent patch of film which has been exposed to background radiation only. This method largely corrects the observed intensity for the rather high background intensity caused by enclosing the crystal in the pyrex capillary. In view of the inevitable loss of accuracy by an unknown amount of absorption of the diffracted beams by the glass of the capillary, no corrections were made for absorption by the crystal or for variation in area of the observed spots arising from the non-uniformity of cross-sections of the crystal.

The main face of the crystal is (001) and the long axis is the *a* axis, so the observed pleochroism with maximum absorption in a direction parallel to the long axis was at first interpreted as implying stacking of molecules in columns parallel to the *a* axis. However, a trial structure based on this arrangement gave poor agreement between observed and calculated *Fh0l* values, and peaks appeared in the corresponding *h0l* Fourier relative electron-density projection where there were no atoms in the trial structure. A second trial structure suggested by this preliminary Fourier synthesis gave better structure-factor agreement for the *h0l* zone and the set of signs so obtained permitted the calculation of a *h0l* relative electron-density map consistent with the trial structure. In this revised view of the structure the molecules are stacked in columns parallel to the [201] axis, marked *A* in Fig. 3. This arrangement is also consistent with the observed pleochroism since, when viewed perpendicular to the (001) face, the directions of the *a* axis and the columns of molecules appear the same.

Fourier projections

The *h0l* Fourier projection was refined in the usual way, the summation being carried out for points at intervals of $a_0/60$ and $c_0/60$. The final electron-density map (Fig. 1) has been put on an absolute scale by comparison of the observed *Fh0l* with the final calculated values, as shown in Table 2. For this projection, the disagreement factor $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ has the value 30·6% excluding all terms for which F_o is zero. Both this high value and the spurious positive ridges on the electron-density map are probably attributable to errors in the observed intensities due to the crystal being enclosed in a capillary tube.

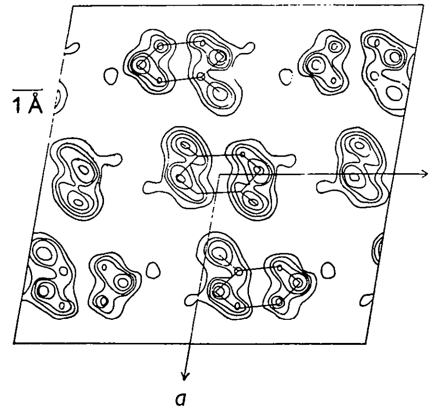


Fig. 1. Fourier projection along the *b* axis. Contours are drawn at 3, 4, 5 and 6 e.Å^{-2}. A quinone molecule and two centro-symmetrically related phenol molecules sandwiching it are outlined.

At this stage it was realized that the structural arrangement is such as to give considerable overlap of atoms for projections on to planes perpendicular to the *a* and *c* axes. It was therefore decided to examine the projection on to the plane perpendicular to the *A* axis of Fig. 3. In this projection each quinone molecule is expected to have two phenol molecules almost exactly superimposed with the C_6 rings in the same orientation and an OH group coinciding with each oxygen atom of the quinone molecule (the two phenol molecules being related by the centre of symmetry at the origin of the unit cell). Although this rules out the possibility of being able to distinguish between the positions of atomic centres in the phenol and quinone molecules it should allow the orientation of the complex molecule as a whole to be determined. Consequently, a set of observed *0kl′* structure factors required for the calculation of this electron density projection was obtained from Weissenberg photographs taken with the crystal oscillating about the *A* axis. The signs were obtained from calculated values of *F0kl′* based on atomic coordinates derived from the *h0l* projection assuming the dimensions of the molecules and the *y* coordinates of the molecular centres. Fig. 2 shows the refined electron density map obtained for this projection, again put on an absolute scale by comparison of observed and calculated *F0kl′* values. The position of one quinone molecule is indicated, and from the absence of extra peaks the expected orientation and position of the phenol molecules is confirmed. That is, the coordinates of the atoms of the phenol molecules as seen in this projection must be approximately the same as those of the quinone atoms, so that the centres of the C_6 rings of the three

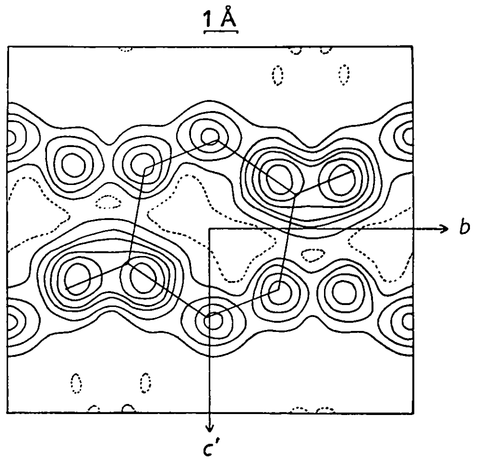


Fig. 2. Fourier projection along the *A* axis. Contours are drawn at 2 e.Å^{-2} (broken line) and at successive intervals of 2 e.Å^{-2}. The position of one quinone molecule is indicated. The two neighbouring phenol molecules are almost exactly superimposed on the quinone in this projection. $c' = c \sin\beta'$, where β' (between *A* and $-c$) = 109°.

components of each complex molecule lie on the same line parallel to the *A* axis. The atoms in the positions of the C=O groups of the quinone molecules do not lie at the centres of the corresponding electron-density peaks because these peaks represent the unresolved positions of these atoms and similar atoms of molecules in adjacent columns. The orientation of the molecules has therefore been deduced from the positions of peaks corresponding to the other atoms of the C_6 rings. The final calculated values of *F0kl′* based on these orientations, when compared with the scaled observed values, give a disagreement factor, $R = 23{\cdot}0\%$ excluding all terms for which F_o is zero.

Table 1. *Atomic coordinates for one structural asymmetric unit*

Group	*x*	*y*	*z*
O	+0·090	−0·357	+0·125
C_1	+0·050	−0·207	+0·073
CH_1	+0·015	+0·015	−0·115
CH_2	+0·060	−0·164	−0·054
OH	+0·238	+0·368	+0·039
C_2	+0·283	+0·185	+0·103
CH_3	+0·272	+0·165	+0·222
CH_4	+0·320	−0·022	+0·281
CH_5	+0·383	−0·185	+0·233
CH_6	+0·395	−0·165	+0·115
CH_7	+0·348	+0·022	+0·048

Description of the structure

From the two Fourier projections the orientation of the molecules is found to be as follows. The projection of the O–O axis of the quinone molecule on to the *bc′* plane perpendicular to the *A* axis makes an angle of 22° with the *b* axis. The O–O axis itself is tilted out of the *bc′* plane by 31°. A second molecular axis in the plane of the ring, but perpendicular to the first, lies in the *bc′* plane. The plane of each phenol molecule is parallel to that of the adjacent quinone molecule and the axis joining OH to the opposite point of the benzene ring is parallel to the O–O axis of quinone. Atomic coordinates consistent with these orientations are shown, for one asymmetric unit, in Table 1, and an orthographic drawing of a unit cell and its contents is shown in Fig. 3.

The structure is seen to be built up of groups of three molecules, each group consisting of a quinone molecule and two centro-symmetrically related phenol molecules so that it constitutes in fact one complex molecule. Within each group the molecules all have the same orientation and are therefore packed plane-to-plane with the quinone sandwiched between the

Table 2. *Comparison of observed and calculated structure factors*

h0l zone

h0l	F_o	F_c
100	22·7	+27·5
$\bar{2}00$	18·0	−14·3
300	99·0	+83·4
600	21·2	−23·7
700	11·6	−13·1
$\bar{1}02$	57·2	+99·0
$\bar{4}02$	17·4	+22·2
$\bar{5}02$	14·6	+14·3
$\bar{6}02$	6·2	− 7·0
$\bar{7}02$	35·2	−40·0
$\overline{10}$,0,2	13·1	−15·2
$\bar{1}04$	5·0	− 3·0
$\bar{2}04$	50·6	−56·0
$\bar{3}04$	10·5	−12·2
$\bar{4}04$	7·3	+ 8·4
$\bar{6}04$	9·3	+ 7·0
$\bar{8}04$	6·8	− 7·9
$\bar{1}06$	4·9	+ 4·8
$\bar{2}06$	13·6	−14·4
$\bar{3}06$	45·9	−94·6
$\bar{4}06$	6·0	− 1·7
$\bar{5}06$	7·0	+ 3·9
$\bar{6}06$	12·7	+16·3
$\bar{9}06$	19·0	+29·6
$\bar{4}08$	6·1	− 2·4
$\bar{7}08$	16·1	+17·1
$\overline{10}$,0,8	24·1	+27·4
$\overline{13}$,0,8	10·5	+ 9·7
$\bar{3}$,0,12	9·7	− 6·6
$\bar{9}$,0,12	7·5	− 9·2
002	20·1	+17·2
102	15·1	−19·1
202	13·6	+29·2
302	20·6	−12·4
402	12·1	+ 6·3
502	5·8	+ 0·3
802	7·0	− 1·3
902	5·1	+ 6·4
004	4·5	− 5·0
104	46·3	−54·0
204	20·0	−11·2
304	4·8	+11·9
504	10·5	+ 3·4
704	17·7	− 6·6
10,0,4	10·4	−15·4
006	32·2	−38·8
106	4·2	− 6·0
406	9·7	+ 3·4
008	8·2	+ 7·0
508	10·2	+ 8·3
808	14·1	+19·1
8,0,10	6·9	+ 3·0
0,0,12	11·8	−14·1

0kl′ zone

0kl′	F_o	F_c
002	11·1	+24·3
004	11·8	−13·6
006	11·3	−11·9
008	2·2	− 1·8
012	4·4	+ 4·0
014	6·8	+ 5·0
016	5·1	+ 4·9
018	3·5	+ 4·0
020	5·0	− 4·5
022	8·0	− 7·6
024	3·9	− 6·8
026	3·1	+ 2·7
028	5·1	+ 5·6
0,2,12	3·0	− 1·6
040	1·8	− 1·6
042	3·0	− 2·6
046	3·2	+ 3·6
048	3·0	+ 3·2
060	5·5	+ 5·7
062	2·5	+ 2·4
064	2·4	− 2·4
066	2·6	− 2·5

two phenol molecules. The groups themselves are arranged in columns parallel to the A axis. Adjacent columns are linked together by hydrogen bonds of length 2·64 Å between each phenolic OH group and an oxygen atom of a quinone molecule in the next column. Two such hydrogen bonds are indicated by broken lines in Fig. 3.

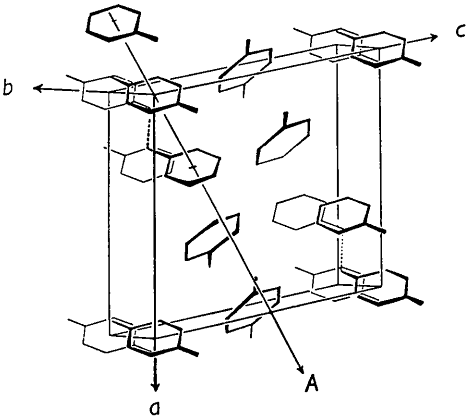


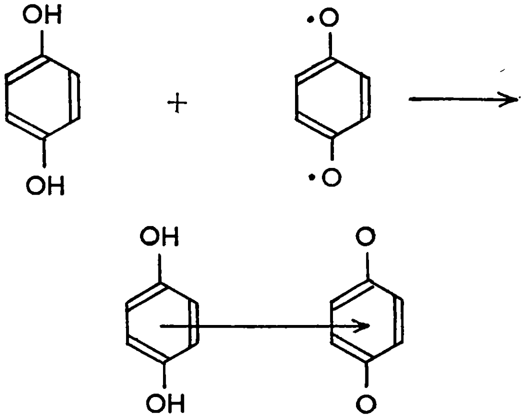
Fig. 3. Orthographic drawing showing the contents of one unit cell, with an additional phenol molecule, to illustrate the sandwiching of the quinone at 0, 0, 0 by phenols at $\frac{1}{3}$, 0, $\frac{1}{6}$ and $\frac{2}{3}$, 0, $\frac{5}{6}$. Such groups of three molecules are stacked in columns parallel to the [201] axis, marked A.

Discussion

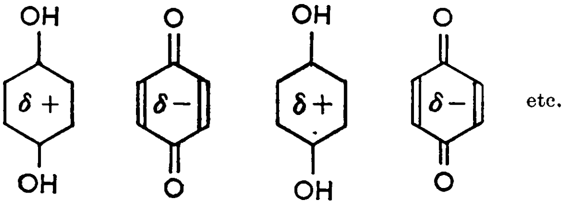
Although the hydrogen-bonding must make an important contribution to the intermolecular forces in the structure, it is the unusual plane-to-plane packing of alternate polarizing and polarizable molecules which is characteristic of this type of molecular complex (Wallwork & Harding, 1953) and which is interpreted as implying polarization bonding between these molecules. It is to be expected that such polarization bonding should be revealed also in a shortening of the van der Waals distances between these molecules. The perpendicular interplanar separation of molecules within each group is 3·33 Å but the shortest distances between actual atomic centres in adjacent molecules are $A/3 = 3{\cdot}87$ Å. It does not appear, therefore, that there is any abnormality in the van der Waals contacts. The same conclusion was reached by Powell, Huse & Cooke (1943) after an investigation of the structure of the molecular compound between *p*-iodoaniline and *s*-trinitrobenzene, except that there may be possible NH_2–NO_2 hydrogen bonds in that structure. However, there is no accurate knowledge of what normal van der Waals distances should be for molecules in a plane-to-plane arrangement, so the observed distances cannot be used either to confirm or to exclude the existence of polarization bonds between the molecules.

Hitherto, the explanations of the existence of molecular complexes in terms of polarization (e.g. Briegleb, 1937; Anderson, 1937) have suggested that the interaction is between a polar group and a polarizable molecule. The evidence of the plane-to-plane structural arrangement in quinhydrones and trinitrobenzene complexes (cf. Powell, Huse & Cooke, 1943) suggests that the interaction is taking place between the π molecular orbitals of alternate polarizing and polarizable molecules. This may be regarded as the formation between the molecules of a partial π-bond of a type suggested by Dewar (1949). For complete molecular π-bond formation it is essential that the 'acceptor' molecule must have a vacant orbital. In quinhydrones this extreme state of affairs could arise by quinone becoming a diradical of benzenoid form:

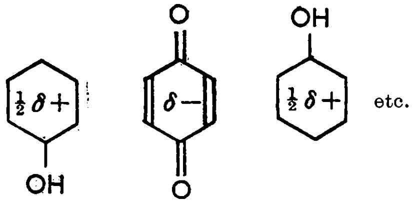
Such a diradical is then capable of receiving an electron pair from the 'donor' molecule with the formation of a molecular π-bond



In this extreme process, a strong intermolecular bond would be formed between pairs of molecules. However, in phenoquinone each quinone molecule is linked by polarization bonds to two phenol molecules, and the bonds are evidently not strong because there is no appreciable shortening of intermolecular distances. In quinhydrone itself there appear to be infinite columns composed of equally spaced alternate quinol and quinone molecules with no tendency to form strong bonds between pairs of molecules. It seems more likely, then, that only partial π-bonds are formed by a partly vacant 'acceptor' orbital receiving a share in electrons from 'donor' orbitals on either side of it. This view has some similarity with both the hypothesis of ionic structures proposed by Weiss (1942, 1943) and with the formulation of the polarization bond suggested by McKeown *et al.* (1951), because there will be a partial transfer of electrons from the 'donor' to the 'acceptor' molecules resulting in such partial ionic structures as The stoichiometric ratio of 2 phenol:1 quinone in solid phenoquinone is therefore presumably caused by the hydrogen-bonding requirements and is not due to the polarization bonding. This view is supported by the evidence (Michaelis & Granick, 1944) that in alcoholic or petrol ether solutions, where presumably the hydrogen-bonding requirements are not so stringent, phenol forms only a 1:1 complex with quinone in the same way as quinol. This implies that in solution both complexes exist as 'partial ion pairs'.



Quinhydrone



Phenoquinone

There is one difficulty in the formulation of quinhydrones as π-complexes. It would be expected that maximum π-orbital overlap would be obtained if the planes of all the molecules in the complex were perpendicular to the line joining their centres. However, the molecules are tilted from this position by about 30° in both phenoquinone and quinhydrone. This distortion of the molecular π-bonds may be explained on the grounds that it is a necessary compromise between efficiency of packing and the formation of the full complement of hydrogen bonds. This explanation is supported by preliminary evidence that in the structure of the chloranil–hexamethylbenzene complex where no hydrogen bonding is possible the molecular planes are perpendicular to the lines joining their centres so that here there is maximum π-bond overlap. Further details of the chloranil–hexamethylbenzene structure will be reported in Part II.

Note added 23 *April* 1953.—Since the preparation of this manuscript, the important papers by Mulliken (1952) and Nakamoto (1952) have come to our notice. These authors also interpret the bonding in this type of molecular compound essentially in terms of π-orbital overlap, and our conclusions appear to be in agreement with the views expressed in these papers.

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