

## The Crystal Structure of 8,8'-dibromo-2,2'-methylenediquinoline

BY J. VAN THUIJL AND C. ROMERS

Laboratory of Organic Chemistry, University of Leiden, The Netherlands

(Received 26 October 1965)

The crystal structure of 8,8'-dibromo-2,2'-methylenediquinoline,  $\text{BrNC}_9\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}_9\text{H}_5\text{NBr}$ , has been determined from three-dimensional X-ray diffraction data collected at  $-180^\circ\text{C}$ . The crystals are orthorhombic; the space group is  $Pbca$  with

$$a = 14.128, b = 7.922, c = 27.741 \text{ \AA}, \text{ and } Z = 8.$$

The structure has been refined by the least-squares method. The final  $R$  value is 13.1% and the standard deviations are of the order of 0.001 Å for the bromine atoms and 0.008 Å and 0.01 Å for the nitrogen and carbon atoms respectively.

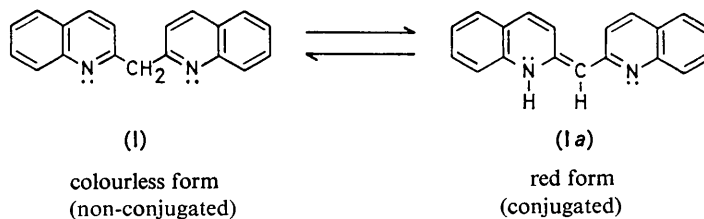
The molecular system is non-conjugated: the central carbon atom is clearly a  $\text{CH}_2$  group connected with C–C bonds of 1.51 Å to the quinoline rings. The C– $\text{CH}_2$ –C valency angle is  $111.5^\circ$  and the dihedral angle between the two planar quinoline rings is  $77^\circ$ .

The observed red colour of the crystals is not in agreement with the firmly established non-planar conformation. It is assumed that the structure is an example of an anomalous mixed crystal in such a way that a small proportion of planar molecules, *viz.* the tautomer  $\text{BrNHC}_9\text{H}_5:\text{CH} \cdot \text{C}_9\text{H}_5\text{NBr}$ , is present in the lattice.

### Introduction

The investigation of the nature of differences between the colourless and the red forms of derivatives of 2,2'-methylenediquinoline forms a part of studies on tautomerism (Havinga & Schors, 1950, 1951; Kraaijeveld & Havinga, 1954*a, b*; Schors, Kraaijeveld & Havinga, 1955; Fischmann, Romers & Umans, 1960; Romers & Umans, 1960; Romers, 1964; van Oijen & Romers, 1966) performed in this laboratory.

Scheibe (1921) discovered that the parent compound 2,2'-methylenediquinoline (I) exists in two forms for which the following structures were initially proposed:

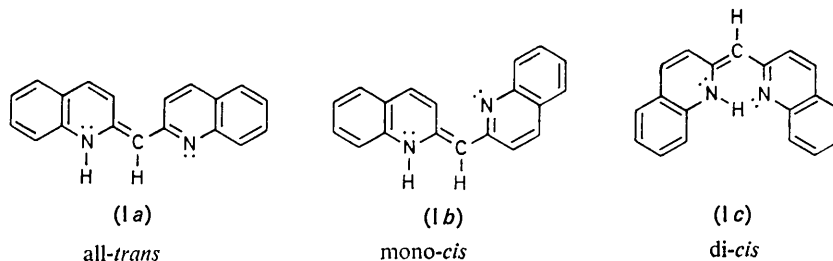


Later Scheibe & Riess (1959) demonstrated that the red form is planar in one of the three possible conformations:

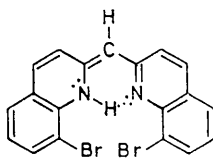
They were able to exclude the all-*trans* form (Ia) and argued that the existence of the mono-*cis* form (Ib) is highly improbable. Further studies by Scheibe and co-workers (Scheibe & Friedrich, 1960; Scheibe, Friedrich & Hohlneicher, 1961; Friedrich & Scheibe, 1961*a*) revealed that the di-*cis* form (Ic), having an intramolecular hydrogen bond, should be the correct representation.

Finally, the correctness of the di-*cis* formula was demonstrated in a crystal structure determination of the red form of 8-bromo-2,2'-methylenediquinoline (van Thuijl, Romers & Havinga, 1963). Unfortunately the red crystals of the monobromo compound are very

small and heavily twinned and it was possible to analyse only one projection of the cell content. The dibromo derivative was obtained in two modifications (van



Thuijl, 1963): colourless, fibrous, polycrystalline material and large, well-developed, red needles. We were not able to obtain proper single crystals from the polycrystalline modification. However, Guinier powder exposures of the two modifications are entirely different and, therefore, it was assumed that the colourless fibres represent a non-planar form and the red needles the planar or nearly planar form (II).



(II)

Moreover, it was interesting to find out whether steric hindrance by the bromine atoms would prevent planarity of the molecule.

### Experimental

The preparation of the compound and an investigation of the space group and cell dimensions were published by van Thuijl, Romers & Havinga (1963). The space group is *Pbca*, with  $a = 14.30^*$ ,  $b = 8.23$ ,  $c = 27.95$  Å at room temperature. The observed density is  $1.61 \text{ g.cm}^{-3}$ , corresponding to  $Z = 8$ . The calculated density is  $1.67 \text{ g.cm}^{-3}$ .

Small red single crystals were selected and enclosed in thin-walled Lindemann-type of glass capillary tube. All X-ray diffraction photographs in this study were taken with  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5418$  Å). During the exposures the crystals were maintained at  $-180^\circ\text{C}$  by means of the cooling equipment described by Altona (1964). Accurate cell dimensions were obtained from zero level Weissenberg photographs about [010] and [001] (unfiltered radiation). These exposures were superposed with aluminum powder lines ( $a = 4.9089$  Å at

$20^\circ\text{C}$ ) at room temperature. Unit-cell dimensions and standard deviations were calculated from 42 measured glancing angles  $\theta$  by means of a least-squares procedure. The values obtained are:  $a = 14.128 \pm 0.001$  Å,  $b = 7.922 \pm 0.005$  Å,  $c = 27.741 \pm 0.001$  Å at  $-180^\circ\text{C}$ .

Complete sets of reciprocal layers for values of  $h$  from 0 to 9 and of  $k$  from 0 to 6, and sets of layers for values of  $l$  from 0 to 4 were collected by means of equi-inclination non-integrated Weissenberg photographs, using nickel-filtered radiation and multiple-film technique. There are 3538 independent reflexions within the limiting sphere, 3344 (94.3%) of which were observed, 465 having zero intensity. The remaining 2879 reflexions were used in the refinement procedure. The intensities were estimated visually and reduced to structure factor moduli (Geise, 1964) applying the usual Lorentz, polarization and spot-shape corrections. The crystals used for exposures about [100], [010], and [001] were cut to blocks with square cross-sections. The linear absorption coefficient for  $\text{Cu } K\alpha$  radiation amounts to  $73.5 \text{ cm}^{-1}$ . In order to correct for absorption the crystals were treated as cylinders with radii of 0.18, 0.12, and 0.20 mm respectively. Finally the structure factor moduli were put on a common scale by means of a scaling procedure given by Rollett & Sparks (1960).

### Determination of the structure

The positions of the bromine atoms were determined from a three-dimensional non-sharpened Patterson function, and used as the basis of a structure factor calculation, resulting in an  $R$  value of 42% for all reflexions. In an attempt to solve the structure from the subsequently computed electron density map, we assumed that the molecule could have either conformation (Ia) or (Ib) or (Ic). However, no molecule having one of these conformations could be placed satisfactorily at the peaks in the density map. Using Br(1) as a starting point (see Fig. 1 for the numbering of the atoms), one quinoline ring, N(1), C(1)  $\cdots$  C(9), could be clearly seen in the map.

\* Previously erroneously stated as 14.9 Å.

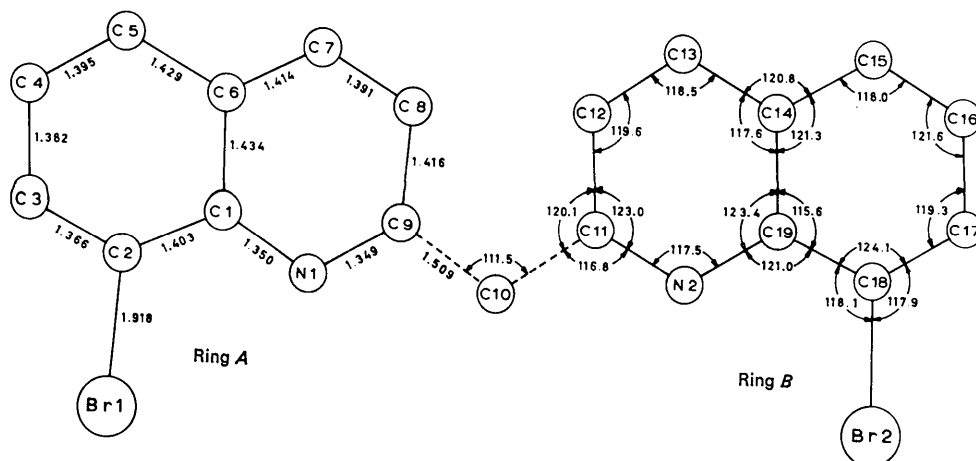


Fig. 1. Numbering of atoms and mean values of bond lengths and angles. (For individual values see Table 3).

It was decided to calculate structure factors with contributions of the bromine atoms and the ten light atoms already located. This calculation resulted in an  $R$  value of 33% and in a second Fourier map 23 peaks per asymmetric unit could distinctly be seen. These maxima however did not correspond to a planar molecule in one of the possible forms (Ia), (Ib), or (Ic), but to a non-planar conformation (I) with a dihedral angle of about  $80^\circ$  between the quinoline rings.

### The refinement

A least-squares method in block-diagonal approximation (Geise, Romers & Rutten, 1966; Rutten, 1966), minimizing  $\sum w(F_o - F_c)^2$ , was used to refine the structure. The weighting factor  $w$  of each reflexion was calculated according to

$$w = (a + F_{\min}) / (a + F_o + b \cdot F_o^2),$$

Table 1. *Final atomic positions and standard deviations* ( $\text{\AA} \times 10^4$ ).

For numbering of atoms see Fig. 1.

	$x/a$	$y/b$	$z/c$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\bar{\sigma}$
Br(1)	0.10730	0.07188	0.17683	11	11	9	10
Br(2)	0.00851	0.33739	0.42032	12	11	11	11
N(1)	0.1772	-0.0887	0.2704	79	72	72	74
N(2)	0.0934	-0.0121	0.4066	88	83	67	79
C(1)	0.2499	-0.0404	0.2432	107	100	77	95
C(2)	0.2355	0.0376	0.1985	91	98	86	92
C(3)	0.3051	0.1006	0.1696	90	99	107	99
C(4)	0.3996	0.0822	0.1837	99	120	105	108
C(5)	0.4237	-0.0033	0.2255	99	113	86	99
C(6)	0.3468	-0.0584	0.2565	103	94	93	97
C(7)	0.3653	-0.1524	0.2985	104	104	100	103
C(8)	0.2913	-0.2047	0.3281	99	100	89	96
C(9)	0.1971	-0.1649	0.3133	91	80	89	87
C(10)	0.1152	-0.2196	0.3435	93	103	85	94
C(11)	0.1254	-0.1647	0.3957	104	81	85	90
C(12)	0.1647	-0.2749	0.4300	115	96	89	100
C(13)	0.1738	-0.2288	0.4773	98	108	102	103
C(14)	0.1460	-0.0624	0.4898	118	93	89	100
C(15)	0.1513	-0.0031	0.5375	105	106	85	99
C(16)	0.1174	0.1575	0.5478	126	113	113	117
C(17)	0.0794	0.2594	0.5138	106	107	98	104
C(18)	0.0706	0.2011	0.4675	102	103	84	96
C(19)	0.1029	0.0412	0.4530	99	103	85	96

Table 2. *Final temperature factor parameters* ( $\text{\AA}^2 \times 10^2$ )

For numbering of atoms see Fig. 1

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{31}$	$B$
Br(1)	3.77	4.46	2.34	0.35	0.20	-0.41	216
Br(2)	4.44	3.69	2.90	0.29	-0.15	0.40	228
N(1)	2.97	2.57	1.94	-0.58	-0.29	-0.22	143
N(2)	4.45	3.11	0.97	0.70	-0.40	0.18	145
C(1)	4.14	3.66	1.48	0.49	-0.55	0.10	161
C(2)	2.77	3.60	2.07	0.47	0.10	-0.09	201
C(3)	1.80	3.29	4.43	0.10	-0.89	0.04	211
C(4)	2.68	5.45	2.80	-1.45	-0.83	0.45	156
C(5)	3.13	5.16	2.33	-0.22	-1.66	0.09	230
C(6)	3.01	3.63	2.85	0.67	-0.72	-0.17	215
C(7)	3.02	4.35	2.70	-0.09	0.08	0.52	206
C(8)	2.53	3.36	3.01	-0.81	0.36	0.83	177
C(9)	2.46	2.42	2.54	-0.18	0.25	-0.49	130
C(10)	3.25	4.17	1.83	-1.15	-0.83	-0.29	201
C(11)	3.67	2.15	1.98	0.09	-0.14	0.04	150
C(12)	4.90	2.90	2.42	-1.12	0.28	-0.06	199
C(13)	2.77	3.92	3.74	-0.40	-0.09	-0.06	209
C(14)	4.24	3.30	2.09	-0.46	0.06	-0.65	189
C(15)	3.63	4.29	1.84	-0.45	0.04	0.09	204
C(16)	4.73	4.49	3.08	-1.93	-0.09	0.54	266
C(17)	3.95	3.80	2.87	0.74	-0.70	-0.21	205
C(18)	3.69	3.73	2.03	-0.18	-0.95	0.03	171
C(19)	3.95	3.88	1.57	-0.10	-1.12	-0.53	173

with  $F_{\min}=0.5$ ,  $a=10$ , and  $b=0.5$ . The scattering factors used were taken from Thomas & Umeda (1957) for bromine, from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and nitrogen, and from McWeeny (1951) for hydrogen. Application of individual isotropic temperature factors led to an  $R$  value of 14.5% in four steps. After six more cycles with anisotropic temperature factors of the form  $\exp[-2\pi^2(h^2a^*U_{11}+2hka^*b^*U_{12}+\dots)]$  the  $R$  value dropped to 13.1%. Hydrogen atoms were introduced at calculated positions but were not refined. They were given isotropic temperature factors equal to those of the corresponding carbon atoms in the last cycle of isotropic refinement. After two more cycles the refinement was considered complete since all shifts were well within the standard deviations,  $R$  still being 13.1%. The final atomic positions are given in Table 1 and the temperature factor parameters in Table 2.

### Discussion of the structure

The bond distances and angles, uncorrected for vibrational effects, are given in Table 3. A comparison of intramolecular bonds in both quinoline moieties of the molecule shows no significant difference between chemically equivalent bond lengths. The same applies for most equivalent bond angles, with the exception perhaps of the angles  $C(6)-C(7)-C(8)$  and  $C(7)-C(8)-C(9)$ . For this reason mean values of bond lengths and angles are given in Fig. 1. Disregarding the bonds  $C(9)-C(10)$  and  $C(10)-C(11)$  the mutual variation of C-C bond lengths (between 1.366 and 1.434 Å) is of the same order as in the molecule  $\alpha$ -phenazine (Herbstein & Schmidt, 1955), and acridine II and acridine III (Phillips, 1956; Phillips, Ahmed & Barnes, 1960). Their mean value (1.403 Å) is the same as found in naphthalene (1.401 Å, Cruickshank & Sparks, 1960),  $\alpha$ -phenazine (1.402 Å), acridine II (1.405 Å), and acridine III (1.404 Å). The mean value of C-N distances (1.344 Å) also compares well with the mean value of 1.345 Å found for the C-N distances found in  $\alpha$ -phenazine, acridine II, and acridine III. In pyrazine (Wheatley, 1957) this mean distance amounts to 1.334 Å, in bis(2,2'-dipyridyliminato)palladium(II) to 1.366 Å (Freeman & Snow, 1965).

The C-N-C bond angle (mean value 117.5°) is consistent with the observation by Hamaka & Liquori (1956) that in  $N$ -heteroaromatic ring systems the bond angle of nitrogen is less than 120°. In pyridine this angle is 117.6° (Liquori & Vaciago, 1956), in pyrimidine (Wheatley, 1960) 115.2°, in pyrazine 115.1°, in acridine II 117.2°, in acridine III 117.8°, and in  $\alpha$ -phenazine 116.6°. On the other hand, the corresponding C-C-C angle in naphthalene (Cruickshank & Sparks, 1960) is 120.2°.

The dimensions of the quinoline rings agree well with those found by Palenik (1964*a*, *b*) in copper- and

\* A complete list of calculated and observed structure factors is available on request.

Table 3. Individual bond lengths and bond angles

Bond lengths		Ring B	
Ring A		Ring B	
Br(1)-C(2)	1.927 Å	Br(2)-C(18)	1.908 Å
N(1)-C(1)	1.333	N(2)-C(19)	1.366
N(1)-C(9)	1.364	N(2)-C(11)	1.333
C(1)-C(2)	1.396	C(18)-C(19)	1.409
C(1)-C(6)	1.435	C(14)-C(19)	1.434
C(2)-C(3)	1.364	C(17)-C(18)	1.368
C(3)-C(4)	1.399	C(16)-C(17)	1.364
C(4)-C(5)	1.401	C(15)-C(16)	1.388
C(5)-C(6)	1.444	C(14)-C(15)	1.414
C(6)-C(7)	1.409	C(13)-C(14)	1.419
C(7)-C(8)	1.398	C(12)-C(13)	1.383
C(8)-C(9)	1.424	C(11)-C(12)	1.408
	C(9)-C(10)	1.505	
	C(10)-C(11)	1.513	
Bond angles		Ring B	
Ring A		Ring B	
C(1)-C(2)-Br(1)	118.3°	C(19)-C(18)-Br(2)	117.8°
C(3)-C(2)-Br(1)	116.2	C(17)-C(18)-Br(2)	119.6
C(1)-C(2)-C(3)	125.5	C(17)-C(18)-C(19)	122.6
C(1)-N(1)-C(9)	117.6	C(11)-N(2)-C(19)	117.4
N(1)-C(1)-C(2)	121.5	N(2)-C(19)-C(18)	120.5
N(1)-C(1)-C(6)	124.2	N(2)-C(19)-C(14)	122.7
C(2)-C(1)-C(6)	114.3	C(14)-C(19)-C(18)	116.8
C(2)-C(3)-C(4)	119.1	C(16)-C(17)-C(18)	119.5
C(3)-C(4)-C(5)	121.1	C(15)-C(16)-C(17)	122.1
C(4)-C(5)-C(6)	117.2	C(14)-C(15)-C(16)	118.8
C(1)-C(6)-C(5)	122.5	C(14)-C(15)-C(19)	120.1
C(5)-C(6)-C(7)	120.6	C(13)-C(14)-C(15)	121.0
C(1)-C(6)-C(7)	116.4	C(13)-C(14)-C(19)	118.7
C(6)-C(7)-C(8)	120.3	C(12)-C(13)-C(14)	116.7
C(7)-C(8)-C(9)	117.8	C(11)-C(12)-C(13)	121.3
C(8)-C(9)-C(10)	120.0	C(10)-C(11)-C(12)	120.2
N(1)-C(9)-C(8)	123.0	N(2)-C(11)-C(12)	123.1
N(1)-C(9)-C(10)	116.8	N(2)-C(11)-C(10)	116.7
	C(9)-C(10)-C(11)	111.5°	

zinc-8-hydroxyquinolinolate. For example the bond  $C(1)-C(6)$  is significantly larger than 1.40 Å; Palenik reports 1.418 Å (1964*a*) and 1.423 Å (1964*b*), compared with our mean value of 1.434 Å.

The bond angle  $C(9)-C(10)-C(11)$  (111.5°) deviates significantly from all other C-C-C bond angles (mean value 119.8°). Its value indicates a 'tetrahedral' bond angle  $R-CH_2-R$  (Davis & Hassel, 1963; Mossel & Romers, 1964; Bucourt & Hainaut, 1965). The lengths of the bonds  $C(9)-C(10)$  (1.505 Å) and  $C(10)-C(11)$  (1.513 Å), in close agreement with the accepted value of 1.501 Å for  $sp^3-sp^2$  bonds (Lide, 1962), are a second indication that C(10) is a methylenic carbon atom.

A third argument in favour of a methylenic atom C(10) was supplied by a difference Fourier synthesis. This synthesis, with contributions of heavy atoms subtracted, showed clearly at expected positions all ten hydrogen atoms attached to the carbon atoms of the quinoline rings, and two hydrogen atoms attached to C(10) at tetrahedral positions.

Both quinoline ring systems (excluding the central carbon atom C(10) and the bromine atoms) are planar according to the following equations (*cf.* Fig. 1):

$$\text{Ring A} - 0.0023X + 0.8778Y + 0.4791Z = 2.9540 \quad (A)$$

$$\text{Ring B} - 0.9039X - 0.3740Y + 0.2075Z = 1.1781. \quad (B)$$

These equations were calculated with respect to an orthogonal coordinate system  $X, Y, Z$  with directions  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  according to the method of Schomaker, Waser, Marsh & Bergman (1959). Table 4 lists the distances of the individual atoms from their respective least-squares planes.

Table 4. Distances ( $\text{\AA}$ ) of atoms from least-squares planes

Atom	Ring A	$d$	Atom	Ring B	$d$
N(1)		-0.02	N(2)		+0.01
C(1)		+0.01	C(19)		-0.01
C(2)		+0.06	C(18)		+0.02
C(3)		+0.01	C(17)		-0.00
C(4)		-0.05	C(16)		+0.01
C(5)		-0.01	C(15)		-0.01
C(6)		-0.04	C(14)		-0.04
C(7)		+0.06	C(13)		+0.03
C(8)		+0.03	C(12)		+0.01
C(9)		-0.06	C(11)		-0.01

The distances from C(10) to the planes  $A$  and  $B$  are 0.08  $\text{\AA}$  and 0.02  $\text{\AA}$  respectively. Br(1) is 0.11  $\text{\AA}$  from plane  $A$  and Br(2) is 0.13  $\text{\AA}$  from plane  $B$  and it can be said that both bromine atoms are significantly outside the planes of their respective quinoline rings. The dihedral angle between planes  $A$  and  $B$  is  $77^\circ$ . The apparent non-planar conformation of the molecule is, of course, a fourth argument in favour of a methylenic central carbon atom. The molecule has the non-planar conformation (I) with approximate symmetry  $C_2$ .

### Packing and colour

In Fig. 2 a projection is given along the  $a$  axis. One molecule, 1, with coordinates  $x, y, z$ , is surrounded by twelve neighbours, contributing 137 intermolecular dis-

tances smaller than 4.0  $\text{\AA}$  to the central molecule. There are eight distances smaller than 3.6  $\text{\AA}$ , the shortest being 3.46  $\text{\AA}$ , between C(14) at  $x, y, z$  and C(18) at  $-x, -y, 1-z$ . Most small distances are between molecules 1 and 2, with coordinates  $\frac{1}{2}-x, \frac{1}{2}+y, z$ , and these contacts account for the good packing in the  $\mathbf{b}$  direction (Fig. 2). The packing parallel to [001] is rather poor; only 21 distances smaller than 4.0  $\text{\AA}$  being found in that direction. The most important contributors to this number are two short Br(1)-Br(2) contacts of 3.66  $\text{\AA}$ : from Br(1) at  $x, y, z$  to Br(2) at  $-x, -\frac{1}{2}+y, \frac{1}{2}-z$  and from Br(2) at  $x, y, z$  to Br(1) at  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ . Packing parallel to [100] is somewhat better; the strongest contacts are from molecule 1 to one with coordinates  $-x, -y, 1-z$ .

It can be concluded that the non-planar conformation of the molecule with a central methylenic carbon atom is firmly established. This conclusion contradicts the optical behaviour of the crystals and considerable time and effort were spent to find an explanation for this phenomenon.

The red colour of the compound in the solid state and in solution is to be attributed to  $\pi \rightarrow \pi^*$ -transitions in the visible part of the spectrum, the strongest absorption being situated at about 510-520  $m\mu$  (subject to solvent effects), with  $\epsilon_{\max} \sim 25000$  (Friedrich & Scheibe, 1961*b*; van Thuijl, 1963; Daltrozzo, Hohlneicher & Scheibe, 1965). The first  $\pi \rightarrow \pi^*$  transition for the quinoline molecule itself is situated in the ultraviolet region of the spectrum:  $\lambda = 316 m\mu$ . The colourless form of 2,2'-methylenediquinoline has its first transition at  $\lambda = 318 m\mu$ ; the spectrum is analogous to that of quinoline itself. It is therefore evident that for transitions in the visible part of the spectrum, conjugation over a methylenic carbon atom C(10) is required in a more or less planar conformation since a non-

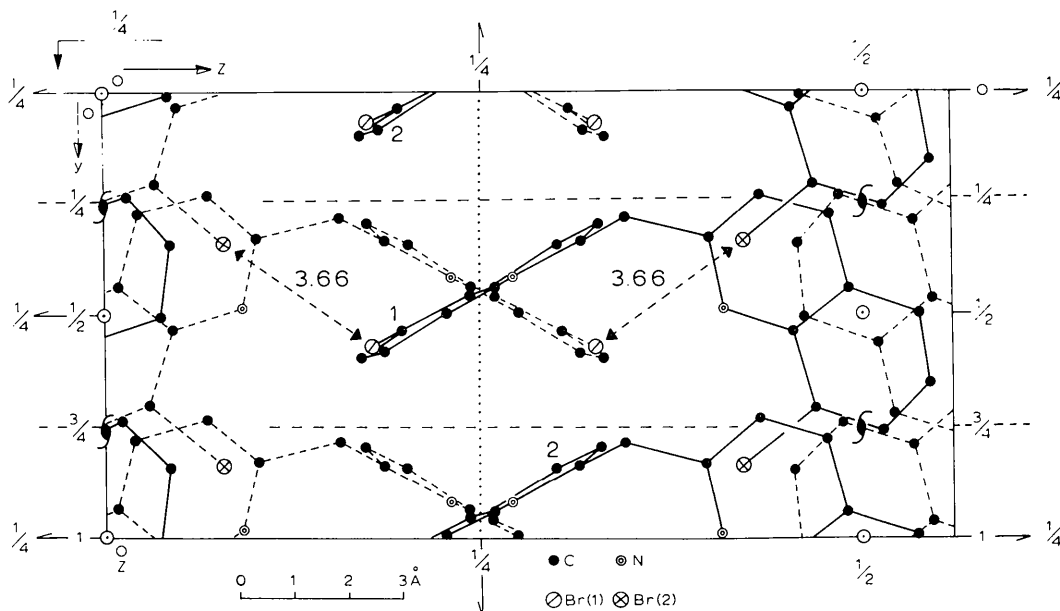


Fig. 2. Part of unit cell viewed along [100].

planar conformation (I), in which conjugation is restricted to the quinoline moieties proper, only has transitions in the ultraviolet region.

Finally we arrived at the conclusion that the red crystals of 8,8'-dibromo-2,2'-methylenediquinoline, mainly consisting of molecules in the non-planar conformation (I), are mixed with planar molecules (presumably in the di-*cis* conformation (Ic), the latter being the cause of the intense red colour. Slow recrystallization of the red crystals gives very thin, *nearly* (but not completely) colourless crystals. The X-ray diffraction patterns of these thin needles are identical with those of the red crystals and differ entirely from the Guinier patterns of the white fibrous product. It seems that the crystal structure of this so-called red form only occurs in the case of incorporation of planar molecules. In absence of planar molecules this crystal structure is not observed; only white fibrous cotton-like crystals appear.

The incorporation of planar guest molecules in the lattice of non-planar host molecules can be accomplished in the form of a solid solution or as anomalous mixed crystals (Neuhaus, 1944). The former possibility requires an undisturbed pattern of bromine atoms, between which non-planar as well as planar molecules can be accommodated in a disordered way. An extensive study does not reveal an obvious way of packing planar molecules in the lattice without heavily disturbing the space group requirements. Moreover, the difference Fourier synthesis does not show any extra density regions for planar molecules. Although there is no direct proof for the occurrence of anomalous mixed crystals, it is remarkable that the crystal structure described collapses in the absence of planar molecules. Knowledge of lattice parameters of the 'pure' planar form would be required to settle this point.

All calculations mentioned were performed on the Electrologica X-1 computer of the Centrale Reken Instituut, University of Leiden.

The authors wish to express their acknowledgement to Prof. Dr E. Havinga for his continuous interest in this investigation and to Dr P. Hartman for helpful discussions.

#### References

- ALTONA, C. (1964). *Acta Cryst.* **17**, 1282.  
 BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.  
 BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. chim. Fr.* p. 1366.  
 CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc. A*, **258**, 270.  
 DALTROZZO, E., HOHLNEICHER, G. & SCHEIBE, G. (1965). *Ber. Bunsenges. Physik. Chem.* **69**, 190.  
 DAVIS, M. & HASSEL, O. (1963). *Acta Chim. Scand.* **17**, 1181.  
 FISCHMANN, E., ROMERS, C. & UMANS, A. J. H. (1960). *Acta Cryst.* **13**, 885.  
 FREEMAN, H. C. & SNOW, M. R. (1965). *Acta Cryst.* **18**, 843.  
 FRIEDRICH, H. J. & SCHEIBE, G. (1961a). *Z. Elektrochem.* **65**, 767.  
 FRIEDRICH, H. J. & SCHEIBE, G. (1961b). *Z. Elektrochem.* **65**, 851.  
 GEISE, H. J. (1964). Thesis, Leiden.  
 GEISE, H. J., ROMERS, C. & RUTTEN, E. W. M. (1966). *Acta Cryst.* **20**, 249.  
 HAMEKA, H. F. & LIQUORI, A. M. (1956). *Proc. Kon. Ned. Akad. Wet. B*, **59**, 242.  
 HAVINGA, E. & SCHORS, A. (1950). *Rec. Trav. chim. Pays-Bas*, **69**, 457.  
 HAVINGA, E. & SCHORS, A. (1951). *Rec. Trav. chim. Pays-Bas*, **70**, 59.  
 HERBSTEIN, F. H. & SCHMIDT, G. M. J. (1955). *Acta Cryst.* **8**, 399.  
 KRAAIJEVELD, A. & HAVINGA, E. (1954a). *Rec. Trav. chim. Pays-Bas*, **73**, 537.  
 KRAAIJEVELD, A. & HAVINGA, E. (1954b). *Rec. Trav. chim. Pays-Bas*, **73**, 549.  
 LIDE, D. R., JR. (1962). *Tetrahedron*, **17**, 125.  
 LIQUORI, A. M. & VACIAGO, A. (1956). *Ric. Sci.* **26**, 1848.  
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.  
 MOSSEL, A. & ROMERS, C. (1964). *Acta Cryst.* **17**, 1217.  
 NEUHAUS, A. (1944). *Z. Kristallogr.* **105**, 161.  
 OIJEN, J. H. VAN & ROMERS, C. (1966). *Acta Cryst.* **20**, 169.  
 PALENIK, G. J. (1964a). *Acta Cryst.* **17**, 687.  
 PALENIK, G. J. (1964b). *Acta Cryst.* **17**, 696.  
 PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 237.  
 PHILLIPS, D. C., AHMED, F. R. & BARNES, W. H. (1960). *Acta Cryst.* **13**, 365.  
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.  
 ROMERS, C. (1964). *Acta Cryst.* **17**, 1287.  
 ROMERS, C. & UMANS, A. J. H. (1960). *Proc. Kon. Akad. Wet. B*, **63**, 32.  
 RUTTEN, E. W. M. (1966). Thesis. To be published.  
 SCHEIBE, G. (1921). *Ber. dtsh chem. Ges.* **54**, 786.  
 SCHEIBE, G. & FRIEDRICH, H. J. (1960). *Z. Elektrochem.* **64**, 720.  
 SCHEIBE, G., FRIEDRICH, H. J. & HOHLNEICHER, G. (1961). *Angew. Chem.* **73**, 383.  
 SCHEIBE, G. & RIESS, W. (1959). *Chem. Ber.* **92**, 2189.  
 SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.  
 SCHORS, A., KRAAIJEVELD, A. & HAVINGA, E. (1955). *Rec. Trav. chim. Pays-Bas*, **74**, 1243.  
 THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.  
 THUIJL, J. VAN (1963). Thesis, Leiden.  
 THUIJL, J. VAN, ROMERS, C. & HAVINGA, E. (1963). *Rec. Trav. chim. Pays-Bas*, **82**, 1026.  
 WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182.  
 WHEATLEY, P. J. (1960). *Acta Cryst.* **13**, 80.