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The Crystal and Molecular Structures of Tyrian Purple (6,6′-Dibromoindigotin) and 2,2′-Dimethoxyindigotin

SINE LARSEN[a] and FRANK WÄTJEN[b]

[a] Department of Physical Chemistry and [b] Department of General and Organic Chemistry (Marine Chemistry Section), The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The crystal and molecular structures of the title compounds have been determined by X-ray diffraction methods. The crystals of 6,6′-dibromoindigotin are monoclinic, space group $P2_1/c$, $Z=2$ with unit cell dimensions $a=12.609$ Å, $b=4.842$ Å, $c=11.611$ Å and $\beta=104.42°$. The structure was solved and refined from diffractometer data to a final R-value of 0.037. 2,2′-Dimethoxyindigotin crystallizes in the monoclinic system, space group $C2/c$, $Z=4$ with the unit cell parameters $a=18.611$ Å, $b=6.191$ Å, $c=16.204$ Å and $\beta=126.48°$. This structure was also determined from diffractometer data and refined to an R-value of 0.044.

The two compounds both possess a center of inversion in the crystalline state. From the corresponding bond lengths in the two structures it appears that the structural changes of the indigo system only occur in the moiety that is directly affected by the oxidation. Comparison of the structure of tyrian purple with that of indigotin shows that the structures are very alike and the indigo system is not perturbed by the bromination.

Tyrian purple or royal purple is one of the most well-known compounds among the numerous natural products reported from marine sources. Its history dates back to antiquity, where it possessed the status of a highly esteemed and extremely expensive dye-stuff.

From a chemical view point the indigo chromophore system has been subject to many investigations. Extensive calculations have, however, often been based on insufficient crystal data. We therefore hope that this paper will clarify some of the uncertainty about the indigo chromophore system.

Previously it was shown that tyriverdin, the natural precursor for tyrian purple, is 2,2′-bis-(methylthio)-6,6′-dibromoindigotin.[1] Attempts to grow suitable crystals for diffraction work of this compound were unsuccessful. Instead a crystal structure determination was undertaken for 2,2′-dimethoxyindigotin to obtain information about the structural changes of the indigo system when cross conjugation between the two indolone rings is prevented.

EXPERIMENTAL

6,6′-Dibromoindigotin was prepared as described in a previous publication.[1] Due to the low solubility of this compound in common solvents, crystals suitable for diffraction work were obtained by sublimation at 10^{-4} mmHg, 300 °C. The crystals are dark violet non-transparent plates. X-Ray diffraction photographs showed that the crystals are monoclinic. The space group is uniquely determined to be $P2_1/c$ from the systematically absent reflections. The density of the crystals was measured by flotation in an aqueous solution of KI and HgI_2.

A single crystal of the size $0.4\times0.22\times0.05$ mm was selected for the data collection performed on a Pickers FACS-1 diffractometer using Zr-filtered Mo$K\alpha$ radiation. The intensities were measured at 22 °C operating the diffractometer in a ω scan mode at a rate of 1° min^{-1}. The scan range of 3° was symmetrical. Background counts were made for 20 s at $2\theta_h=2\theta_o+1.8+0.346\tan\theta$ and $2\theta_l=2\theta_o-1.5-0.346\tan\theta$, where $2\theta_o$ is the calculated peak position. The intensities were recorded for all the reflections in the hemisphere ($h\geq0$) in the range $2.4°<2\theta\leq55°$. Three standard reflections were measured after every 60 reflections. The data were corrected for Lorentz, polarization and absorption effects. The symmetry related reflections were averaged to give 1579 independent reflections of

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which the 1169 which had $I/\sigma(I) \geq 2.0$ were classified as observed.

2,2'-Dimethoxyindigotin was synthesized as described previously.[2] After a chromatographic purification ($SiO_2/CHCl_3$) suitable crystals were obtained by evaporation from chloroform. The compound crystallizes as yellow prisms. X-Ray diffraction photographs showed that the crystals are monoclinic. The space group was determined to be either $C2/c$ or Cc from the systematically absent reflections. The density was determined by flotation in an aqueous solution of KI and HgI_2.

A single crystal of the size $0.325 \times 0.18 \times 0.0075$ mm was used for the collection of intensity data with a Picker FACS-1 diffractometer. In this case Mo$K\alpha$ radiation monochromatized from a highly mosaic graphite crystal was used. A $\theta,2\theta$ scan from $2\theta_l = 2\theta_0 - 1.0 - 0.346 \tan\theta$ to $2\theta_h = 2\theta_0 + 1.2 + 0.346 \tan\theta$ was performed at a rate of $1° \text{ min}^{-1}$ in 2θ. Background counts were made for 20 s at each end of the scan range. To check the experimental stability the intensities of five standard reflections were measured after every 50 reflections. All the reflections in the hemisphere ($h \geq 0$) which had $2.4° \leq 2\theta \leq 55°$ were measured and corrected for Lorentz and polarization effects. After averaging of the symmetry related reflections 2010 independent reflections were obtained. Of these 1496 had intensities with $I/\sigma(I) \geq 2.0$ and were classified as observed.

DETERMINATION AND REFINEMENT TO THE STRUCTURES

Both structures were solved and refined by conventional methods using the observed reflections. 6,6'-Dibromoindigotin was solved by the heavy atom method. The position of the bromine atom was deduced from the three dimensional Patterson function and the other nonhydrogen atoms were located by Fourier syntheses. The structure of 2,2'-dimethoxyindigotin was solved by direct methods using the program system MULTAN.[3] On the assumption that the correct space group is $C2/c$ a standard run revealed the positions of all the nonhydrogen atoms in the structure.

The structures were refined by the method of least squares minimizing $\Sigma w\{|F_o| - |F_c|\}^2$. The hydrogen atoms were located in difference Fourier maps calculated after anisotropic refinement of the heavier atoms. The positional parameters for the hydrogen atoms were included in the final cycles of the least squares refinement. For 6,6'-dibromoindigotin a fixed isotropic temperature factor was used for the hydrogen atoms whereas individual isotropic thermal parameters were included in the refinement of the 2,2'-dimethoxyindigotin structure. The weights used in the final refinement cycles follow the expression $w^{-1} = A\sigma(F)^2 + B|F|$. The numerical values for A and B were obtained as described by Nielsen.[4] For 6,6'-dibromoindigotin the values were $A = 1.0$, $B = 0.033$ and for 2,2'-dimethoxyindigotin, $A = 2.0$, $B = 0.030$. In the last cycle of least squares refinement of the 6,6'-dibromoindigotin structure the minimum shift of parameters was 0.4σ and the unit weighted and weighted residuals, R and R_w, came out 0.037 and 0.043. For the 2,2'-dimethoxyindigotin structure the maximum shift of parameters was 0.12σ and the final residuals were $R = 0.044$ and $R_w = 0.047$.

The following computer programs were used: The Vanderbilt system[5] for diffractometer operations, a data reduction program of local origin, ORTEP II[6] for the illustrations, and the X-ray system[7] for the crystal structure analysis.

The atomic scattering factors were taken from Cromer and Mann[8] for C, N, O, and Br and from Stewart *et al.*[9] for H. The anomalous dispersion corrections added to the scattering factor for bromine were those calculated by Cromer and Liberman.[10]

Listings of observed and calculated structure amplitudes may be obtained from the authors.

CRYSTAL DATA

6,6'-Dibromoindigotin; $C_{16}H_8N_2O_2Br_2$; M = 420.07. Monoclinic, $a = 12.609(16)$ Å, $b = 4.842(2)$ Å, $c = 11.611(12)$ Å, $\beta = 104.42(6)°$; $V = 686.53$ Å^3; $D_m = 1.96$ g/cm^3; $Z = 2$; $D_x = 2.032$ g/cm^3. μ(Mo$K\alpha$) = 58.5 cm^{-1}. $F(000) = 408$. Space group $P2_1/c$. The plate face is {100}. Developed forms {100}, {011} and {010}.

2,2'-Dimethoxyindigotin; $C_{18}H_{16}N_2O_4$; M = 324.33. Monoclinic, $a = 18.611(11)$ Å, $b = 6.191(2)$ Å, $c = 16.204(11)$ Å, $\beta = 126.48(3)°$; $V = 1505.15$ Å^3; $D_m = 1.45$ g/cm^3; $Z = 4$; $D_x = 1.431$ g/cm^3. μ(Mo$K\alpha$) = 0.97 cm^{-1}. $F(000) = 680$. Space group $C2/c$. The prismatic crystals are elongated along b.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

The final positional and thermal parameters for 6,6'-dibromoindigotin and 2,2'-dimethoxyindigotin are given in Table 1 and Table 2, respectively. Fig. 1

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations for 6,6′-dibromoindigotin. The expressions for the temperature factors are $\exp\{(-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{23}klb^*c^*)\}$ for the anisotropic and $\exp(-8\pi^2 U \sin\theta^2/\lambda^2)$ for the isotropic ones. The thermal parameters are in units of $Å^2 \times 10^{-2}$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.42643(4)	0.03890(11)	0.15096(5)	4.11(3)	3.89(3)	4.49(3)	0.96(3)	0.68(2)	0.01(2)
N	0.0890(3)	0.7286(9)	0.0856(3)	3.6(2)	3.5(2)	2.55(18)	0.64(18)	1.26(17)	0.32(17)
C2	0.0430(4)	0.9154(9)	−0.0011(4)	2.9(2)	3.0(2)	2.7(2)	0.00(19)	0.80(17)	−0.11(17)
C3	0.1020(4)	0.8995(10)	−0.0972(4)	3.6(3)	3.1(3)	2.7(2)	−0.3(2)	1.05(18)	−0.43(18)
C4	0.1863(4)	0.6939(10)	−0.0565(4)	3.4(3)	3.3(3)	3.0(2)	0.1(2)	1.05(19)	0.07(19)
C5	0.2704(4)	0.5950(11)	−0.1044(4)	4.2(3)	4.0(3)	2.9(2)	0.4(2)	1.3(2)	0.1(2)
C6	0.3403(4)	0.3988(11)	−0.0432(4)	3.9(3)	4.0(3)	4.1(3)	0.8(2)	1.9(2)	−0.5(2)
C7	0.3264(4)	0.3051(9)	0.0664(4)	3.5(3)	2.8(2)	3.3(2)	0.3(2)	0.37(19)	−0.25(19)
C8	0.2447(4)	0.3944(10)	0.1170(4)	3.9(3)	2.9(2)	2.8(2)	0.4(2)	0.83(19)	0.32(18)
C9	0.1747(4)	0.5950(9)	0.0541(4)	3.0(2)	2.8(2)	3.2(2)	−0.39(19)	0.91(18)	−0.30(18)
O1	0.0806(3)	1.0401(7)	−0.1891(3)	4.4(2)	4.0(2)	3.0(2)	0.79(17)	1.23(14)	0.40(14)
				U (restricted)					
H1	0.075(4)	0.704(11)	0.139(4)	3.0					
H2	0.276(4)	0.662(10)	−0.183(4)	3.0					
H3	0.394(4)	0.327(10)	−0.070(4)	3.0					
H4	0.240(4)	0.316(10)	0.194(4)	3.0					

Table 2. Final fractional coordinates and thermal parameters with estimated standard deviations for 2,2′-dimethoxyindigotin. Given as in Table 1.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	0.30132(10)	0.1013(2)	0.12489(10)	3.65(7)	2.91(7)	2.50(6)	−0.58(6)	1.80(6)	−0.08(6)
O1	0.35673(10)	0.5965(2)	0.06871(10)	6.71(9)	3.91(8)	4.10(7)	−1.96(7)	3.25(7)	−0.39(6)
O2	0.34277(7)	0.1369(2)	0.01136(8)	3.11(6)	4.24(7)	2.84(6)	0.05(5)	1.84(5)	−0.42(5)
C2	0.29822(10)	0.2309(3)	0.04823(11)	3.06(8)	2.73(8)	2.42(7)	−0.41(6)	1.69(6)	−0.27(6)
C3	0.34097(11)	0.4492(3)	0.10539(12)	3.16(8)	3.09(8)	2.68(7)	−0.55(7)	1.61(6)	−0.32(6)
C4	0.35664(10)	0.4313(3)	0.20416(12)	2.93(8)	3.45(9)	2.44(7)	−0.06(7)	1.40(6)	−0.38(7)
C5	0.39153(12)	0.5798(3)	0.28420(14)	3.78(9)	4.09(10)	3.28(8)	0.26(8)	1.54(8)	−0.86(8)
C6	0.39543(13)	0.5208(4)	0.36878(14)	4.60(10)	5.97(14)	2.81(9)	1.00(10)	1.63(8)	−1.20(9)
C7	0.36579(13)	0.3180(4)	0.37326(14)	4.24(10)	6.94(15)	2.67(8)	1.83(10)	2.14(8)	0.54(9)
C8	0.33196(12)	0.1671(3)	0.29529(13)	3.22(8)	5.28(12)	2.72(8)	0.79(8)	1.84(7)	0.82(8)
C9	0.32839(10)	0.2262(3)	0.20970(11)	2.43(7)	3.68(9)	2.25(7)	0.39(6)	1.22(6)	0.09(6)
C10	0.43470(12)	0.0896(4)	0.08948(15)	3.11(9)	4.85(12)	4.20(10)	0.07(8)	1.94(8)	−0.29(9)
				U					
H1	0.2645(14)	−0.013(4)	0.1051(16)	4.8(6)					
H2	0.4117(14)	0.720(4)	0.2782(15)	4.8(6)					
H3	0.4201(15)	0.622(4)	0.4264(17)	5.7(6)					
H4	0.3673(14)	0.278(4)	0.4309(17)	5.1(6)					
H5	0.3096(14)	0.025(4)	0.2987(15)	4.3(5)					
H6	0.4665(16)	0.221(4)	0.1245(18)	6.4(7)					
H7	0.4597(16)	0.029(4)	0.0548(17)	6.2(7)					
H8	0.4412(16)	−0.010(4)	0.1406(18)	6.4(7)					

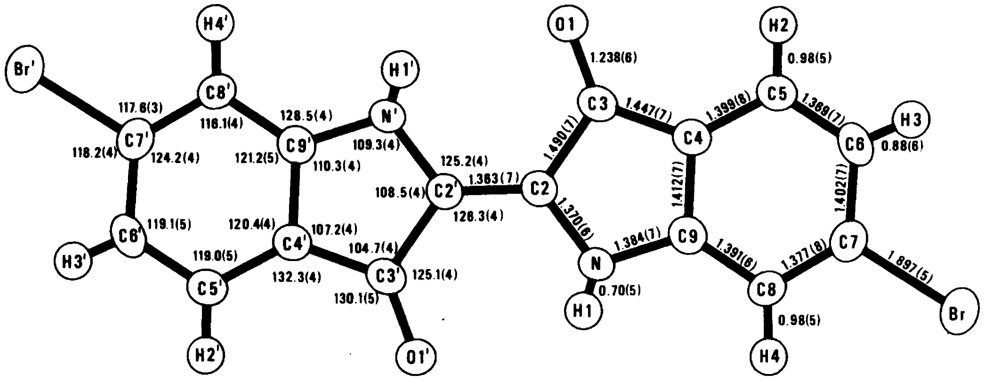

Fig. 1. An ORTEP drawing of 6,6′-dibromoindigotin illustrating the atomic labelling, the bond lengths (Å) and bond angles (deg.). The thermal ellipsoids are scaled to include 50 % probability.

shows the bond lengths and bond angles as well as the molecular structure for 6,6′-dibromoindigotin. The molecular geometry of 2,2′-dimethoxyindigotin is illustrated by the ORTEP drawing in Fig. 2. The bond lengths and bond angles are listed in Table 3.

The crystallographic symmetry implies that both molecules possess a center of inversion. This makes it easier to compare the two structures with respect to the structural changes caused by the oxidation of the indigotin ring system. An inspection of Table 3 and Fig. 1 shows that only the dimensions of the N−C2−C3 moiety have changed. The C2−C3 distance is increased from 1.490 Å to 1.562 Å and

Table 3. Bond lengths (Å) and angles (deg) with estimated standard deviations for 2,2′-dimethoxyindigotin.

Bond lengths		Bond angles	
N−C2	1.451(3)	C9−N−H1	123(2)
C2−C2′	1.547(2)	H1−N−C2	120(2)
C2−O2	1.406(3)	C9−N−C2	110.3(2)
C2−C3	1.562(2)	C3−C2−N	103.0(2)
C3−O1	1.216(3)	N−C2−C2′	112.3(2)
C3−C4	1.450(3)	C3−C2−C2′	110.1(2)
C4−C9	1.398(3)	C3−C2−O2	112.8(2)
C4−C5	1.395(3)	C2′−C2−O2	105.1(2)
C5−C6	1.378(4)	N−C2−O2	113.7(2)
C6−C7	1.392(4)	O1−C3−C2	123.0(2)
C7−C8	1.385(3)	O1−C3−C4	130.4(2)
C8−C9	1.397(3)	C2−C3−C4	106.6(2)
C9−N	1.384(3)	C3−C4−C9	107.7(2)
O2−C10	1.431(2)	C3−C4−C5	130.7(2)
N−H1	0.90(2)	C5−C4−C9	121.6(2)
C5−H2	0.97(3)	C6−C5−C4	118.0(2)
C6−H3	0.98(2)	C5−C6−C7	120.2(2)
C7−H4	0.95(3)	C6−C7−C8	122.7(2)
C8−H5	0.99(2)	C7−C8−C9	117.1(2)
C10−H6	0.97(3)	C8−C9−N	127.8(2)
C10−H7	0.99(3)	C8−C9−C4	120.3(2)
C10−H8	0.98(3)	C4−C9−N	111.9(2)
		C2−O2−C10	114.2(2)

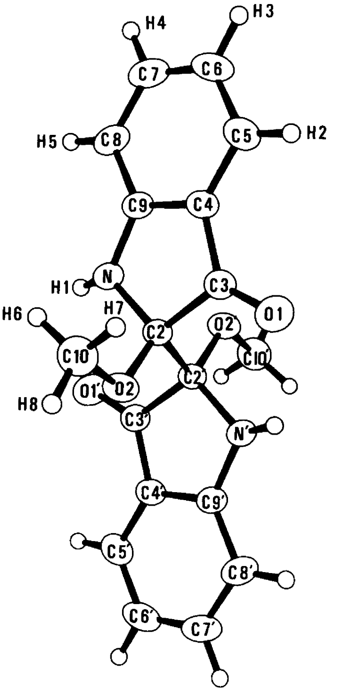

Fig. 2. An ORTEP drawing of 2,2′-dimethoxyindigotin. The thermal ellipsoids for the non-hydrogen atoms are scaled to include 50 % probability.

Table 4. Distances (Å) from least-squares planes. The atoms used to define the plane are marked with *.

6,6′-Dibromoindigotin		2,2′-Dimethoxyindigotin	
N	0.049	N	0.072
C2	0.074	C2	−0.092
C3	0.022	C3	−0.062
C4*	−0.003	C4*	−0.010
C5*	0.001	C5*	0.005
C6*	−0.003	C6*	0.002
C7*	0.006	C7*	−0.004
C8*	−0.007	C8*	−0.001
C9*	0.006	C9*	0.008
O1	0.021	O1	−0.069
H1	0.078	H1	−0.190
Br	0.039		

similarly the C2−N distance of 1.370 Å in 6,6′-dibromoindigotin has changed to 1.451 Å in 2,2′-dimethoxyindigotin. The structural changes caused by the oxidation are also apparent from the calculation of least squares planes shown in Table 4. Whereas 6,6′-dibromoindigotin is strictly planar, the five membered pyrrolidinyl ring in 2,2′-dimethoxyindigotin is puckered. The hydrogen atom bonded to the nitrogen atom lies in the plane of the indolone ring system in 6,6′-dibromoindigotin, but the corresponding hydrogen atom in 2,2′-dimethoxyindigotin is displaced 0.38 Å from the plane defined by C2, N and C9 indicating that the nitrogen atom has a pyramidal configuration in this structure. The variations in molecular dimensions of the remaining part of the ring system are small.

The crystal structure determinations for indigotin and related compounds were performed some 25 years ago by Eller[11] and Gribova[12] and the uncertainties in bond lengths and bond angles make a detailed comparison between the structure of indigotin and 6,6′-dibromoindigotin difficult. The bond lengths and bond angles for 6,6′-dibromoindigotin agree best with the structural results reported by Gribova *et al.*[12] and there are no significant differences between this structure and the present results for 6,6′-dibromoindigotin. We conclude that the bromination of indigotin does not cause significant structural changes of the indigo ring system. The crystal packing is also very similar in the two related structures. In 6,6′-dibromoindigotin it is determined by hydrogen bonds as illustrated in the stereo pair shown in Fig. 3. The molecules related by the twofold screw axis are linked together by the hydrogen bond, N−H1···O1, the N−O1 distance being 2.89 Å and N−H1−O angle is 154°. Exactly the same packing and hydrogen bond pattern is found in the structure of indigotin.[11,12]

The crystal packing of 2,2′-dimethoxyindigotin shown in Fig. 4 is determined by van der Waals interactions. The two methoxy groups apparently cause a steric hindrance for the formation of hydrogen bonds.

The intense colours of the indigoid dyes are intriguing to both theoretical and structural chemists. The PPP- calculations by Klessinger and Lüttke[13] showed that the structure of indigotin could be interpreted as a resonance hybrid of the forms a, b and c depicted in Fig. 5, similar to the merocyanines. According to this interpretation one would expect an elongation of the C2−C2′ double bond nad of the C−O bond together with a shortening of the C2−N and C2−C3 bonds. In 6,6′-dibromoindigotin the C2−C2′ distance of 1.363 Å is significantly longer than the standard ethylenic value of 1.333 Å[14] and one could argue that the C−O distance is also slightly elongated. However, the C2−C3 and C2−N bond lengths correspond to the normal values. On the basis of these observations we conclude that to interpret the electronic

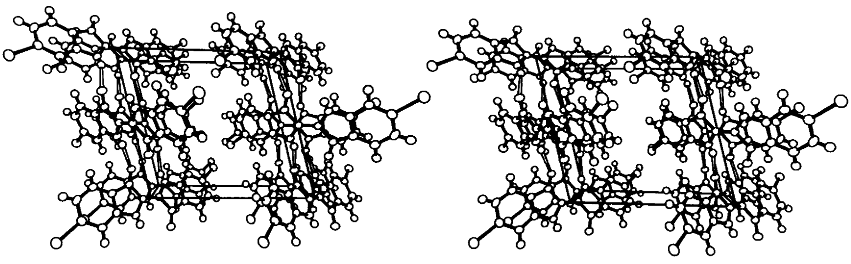

Fig. 3. Stereo pair of 6,6′-dibromoindigotin showing the hydrogen bonds viewed along the *b*-axis.

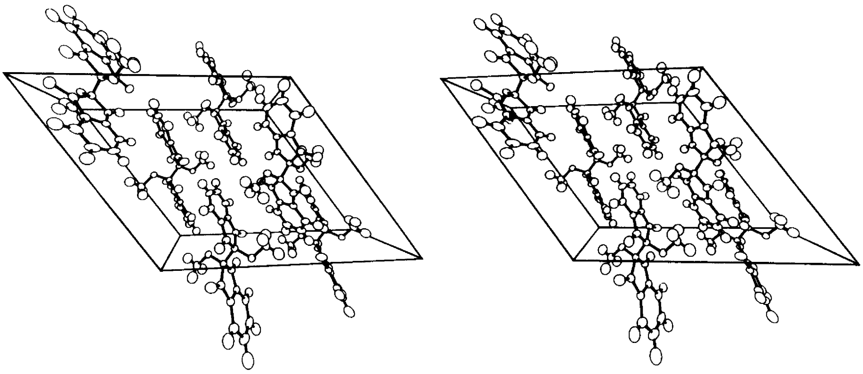

Fig. 4. Stereo pair of 2,2′-dimethoxyindigotin illustrating the packing viewed along the *b*-axis.

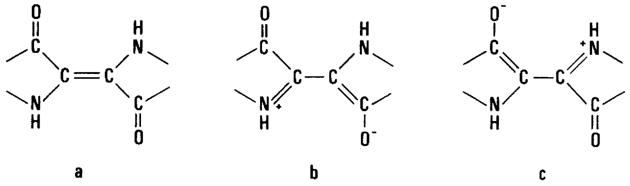

Fig. 5. Resonance structures for the central part at the indigo chromophore.

structure of indigotin as a cross conjugated merocyanine-like system is too simple a picture. Ammon and Hermann, who in their studies of the thioindigo chromophore determined the crystal structure for *trans*-$\Delta^{2,2}$-bis(4,4-dimethylthiolan-3-one), reached the same conclusion for the thioindigo system.[15]

The colour difference between indigotin and tyrian purple corresponds to a shift in the absorption maximum from 604 nm to 590 nm. A similar hypsochromic shift has been observed for other 6,6′-substitution products of indigotin and has been explained as a mesomeric effect as the bromine is *para* to the carbonyl group.

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