Dyes and Pigments 4 (1983) 163–169

Crystal and Molecular Structure of Ciba Yellow 3G

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(Received: 23 March, 1982)

SUMMARY

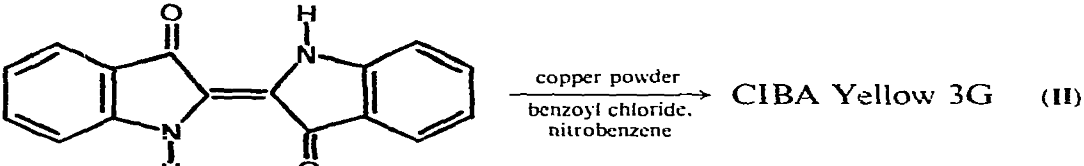
The disputed structure of CIBA Yellow 3G (**II**) *has now been confirmed with the aid of X-ray structure analysis:*

$C_{23}H_{12}N_2O_2$, *Monoclinic*, $P2_1/n$, $a = 20{\cdot}794$ Å, $b = 4{\cdot}755$ Å, $c = 17{\cdot}311$ Å, $\beta = 112{\cdot}09°$, $Z = 4$.

The structure was solved by direct methods and refined to $R = 0{\cdot}079$.

1. INTRODUCTION

CIBA Yellow 3G (**II**) is a vat dye first prepared by Engi[1] by the action of benzoyl chloride, copper powder, and nitrobenzene on indigo (**I**):

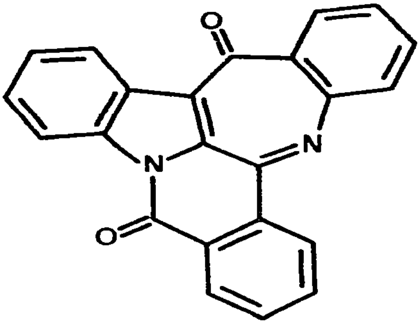


(**I**)

A number of structures have been proposed by various authors on the basis of degradation reactions.[2] Formula **II** represents the structure of CIBA Yellow 3G proposed by H. de Diesbach. Our aim was to provide

Dyes and Pigments 0143-7208/83/$03·00 © Applied Science Publishers Ltd, England, 1983. Printed in Great Britain

unambiguous proof of the structure with the help of X-ray structure analysis.



(II)

2. EXPERIMENTAL

2.1. Data collection

X-ray intensities were measured on an automatic Philips PW 1100 diffractometer, with graphite monochromated CuKα radiation. A single crystal with dimensions 0·5 mm × 0·15 mm × 0·05 mm was used for collecting the intensities of 1832 independent reflections ($3° < \theta < 53°$) in the θ–2θ scan mode. Of these 899 were considered as observed according to the criterion $I > 2\sigma(I)$, and used for the refinement step. Three reflections were monitored every 2 h during the data collection and showed no crystal decomposition. The intensities were corrected for Lorentz and polarisation factors, but not for absorption.

2.2. Structure determination and refinement

The structure was solved by direct methods using first the MULTAN 77 system of programs.[3] From 200 reflections with $E = 1{\cdot}36$, 32 sets of phases were obtained. The E-map corresponding to the phase set with the highest figure of merit (2·92) showed a planar six-membered ring. It soon became obvious that it must have the wrong position in the unit cell. A new attempt to solve the structure with the MULTAN 78 system of programs using the six-membered ring as an atom group of known orientation and random position was successful. The *E*-map corresponding to the phase set with the highest figure of merit (2·95) revealed all non-hydrogen atoms. The value of *R* at this stage was 0·30.

Two cycles of full matrix least-squares refinement of positions and isotropic temperature factors gave $R = 0·139$. This was reduced to 0·089 after three subsequent cycles of anisotropic refinement. At this stage the positions of the hydrogen atoms were calculated from geometrical considerations. With these positions fixed and constant *B* values of 4·0 Å^2, two cycles of refinement yielded $R = 0·079$. The final atomic parameters are given in Tables 1 and 2.

TABLE 1
Fractional Atomic Coordinates of Non-Hydrogen Atoms

Atom	*X/A*	*Y/B*	*Z/C*
N(1)	0·3598(5)	0·351(3)	0·5263(7)
C(2)	0·4322(6)	0·410(3)	0·5678(8)
O(3)	0·4733(4)	0·289(2)	0·5467(5)
C(4)	0·4519(7)	0·628(3)	0·6342(8)
C(5)	0·5247(7)	0·688(3)	0·6651(9)
C(6)	0·5445(7)	0·887(3)	0·7300(8)
C(7)	0·5009(7)	1·028(3)	0·7593(9)
C(8)	0·4290(7)	0·987(4)	0·7283(9)
C(9)	0·4093(7)	0·792(3)	0·6617(9)
C(10)	0·3329(7)	0·712(3)	0·6176(8)
N(11)	0·2837(5)	0·811(3)	0·6369(7)
C(12)	0·2109(7)	0·788(3)	0·6083(9)
C(13)	0·1915(7)	0·993(3)	0·6571(9)
C(14)	0·1225(7)	1·006(3)	0·6456(9)
C(15)	0·0729(7)	0·850(3)	0·5804(8)
C(16)	0·0935(7)	0·666(3)	0·5329(9)
C(17)	0·1634(7)	0·633(3)	0·5413(9)
C(18)	0·1775(7)	0·424(3)	0·4848(9)
O(19)	0·1268(5)	0·306(2)	0·4359(6)
C(20)	0·2469(7)	0·346(3)	0·4939(8)
C(21)	0·2593(7)	0·157(3)	0·4363(8)
C(22)	0·2123(7)	−0·025(3)	0·3721(9)
C(23)	0·2496(6)	−0·191(3)	0·3373(8)
C(24)	0·3220(7)	−0·187(3)	0·3567(9)
C(25)	0·3683(6)	−0·013(3)	0·4245(8)
C(26)	0·3305(7)	0·143(3)	0·4592(8)
C(27)	0·3044(7)	0·478(3)	0·5474(8)

TABLE 2
Fractional Atomic Coordinates of Hydrogen Atoms

Atom	*X/A*	*Y/B*	*Z/C*
H(5)	0·558	0·566	0·645
H(6)	0·597	0·950	0·758
H(7)	0·521	1·173	0·808
H(8)	0·398	1·101	0·753
H(13)	0·230	1·099	0·706
H(14)	0·106	1·152	0·680
H(15)	0·020	0·860	0·571
H(16)	0·056	0·552	0·485
H(22)	0·158	−0·009	0·356
H(23)	0·223	−0·335	0·290
H(24)	0·344	−0·323	0·326
H(25)	0·422	−0·013	0·438

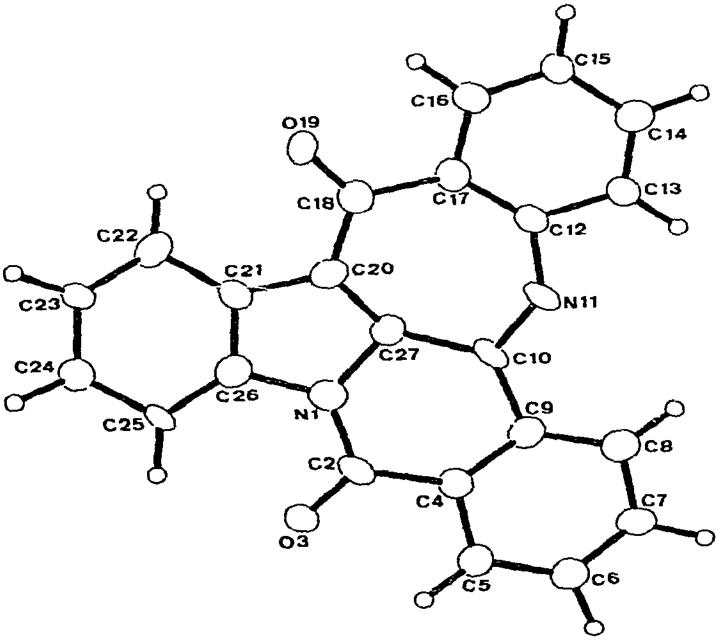


Fig. 1. Perspective view of the molecule with the atomic numbering scheme

3. DISCUSSION

An ORTEP[4] drawing of the molecule showing thermal ellipsoids at 20 % probability and atomic numbering is given in Fig. 1. Bond distances for non-hydrogen atoms are summarized in Table 3.

Within the limits of accuracy, the calculated distances and angles are in agreement with the expected values, although the N_1–C_2 distance is

TABLE 3
Bond Lengths

Bond	*Length* (Å)
N(1)—C(2)	1·43(2)
N(1)—C(26)	1·47(2)
N(1)—C(27)	1·46(2)
C(2)—O(3)	1·20(2)
C(2)—C(4)	1·49(2)
C(4)—C(5)	1·43(2)
C(4)—C(9)	1·39(2)
C(5)—C(6)	1·41(2)
C(6)—C(7)	1·37(2)
C(7)—C(8)	1·40(2)
C(8)—C(9)	1·42(2)
C(9)—C(10)	1·53(2)
C(10)—N(11)	1·28(2)
C(10)—C(27)	1·59(2)
N(11)—C(12)	1·41(2)
C(12)—C(13)	1·44(2)
C(12)—C(17)	1·41(2)
C(13)—C(14)	1·37(2)
C(14)—C(15)	1·42(2)
C(15)—C(16)	1·37(2)
C(16)—C(17)	1·41(2)
C(17)—C(18)	1·50(2)
C(18)—O(19)	1·21(2)
C(18)—C(20)	1·44(2)
C(20)—C(21)	1·43(2)
C(20)—C(27)	1·36(2)
C(21)—C(22)	1·46(2)
C(21)—C(26)	1·38(2)
C(22)—C(23)	1·39(2)
C(23)—C(24)	1·41(2)
C(24)—C(25)	1·46(2)
C(25)—C(26)	1·37(2)

somewhat long for a lactam C–N bond. The C_{20}–C_{27} distance of 1·36 Å is only slightly greater than the length of an isolated carbon–carbon double bond (1·33 Å), whilst the C_{10}–N_{11} distance is with 1·29 Å, in the upper region of the lengths of a carbon–nitrogen double bond (1·24–1·29 Å).

The molecule is almost planar, the greatest deviation from planarity in the whole molecule being 0·06 Å by the C_5 carbon atom. The packing is given by the van der Waals contacts. In Fig. 2, the four molecules of a unit cell are projected on to the (*a*, *c*) plane. No short intermolecular distances are observable.

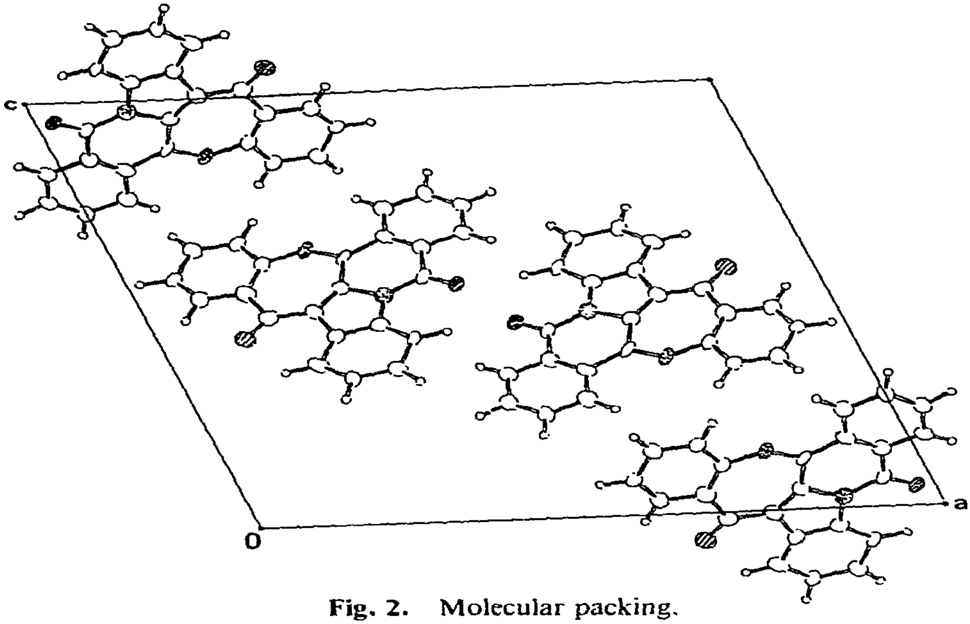


Fig. 2. Molecular packing.

ACKNOWLEDGEMENT

We thank Dr H. H. Bosshard for the initiation of this programme.

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