203. The Reaction of 4-Oxo-4*H*-[1]benzopyran-3-carbaldehyde with 1,2-Benzenediamine. X-Ray Structure Analysis of the Reaction Product

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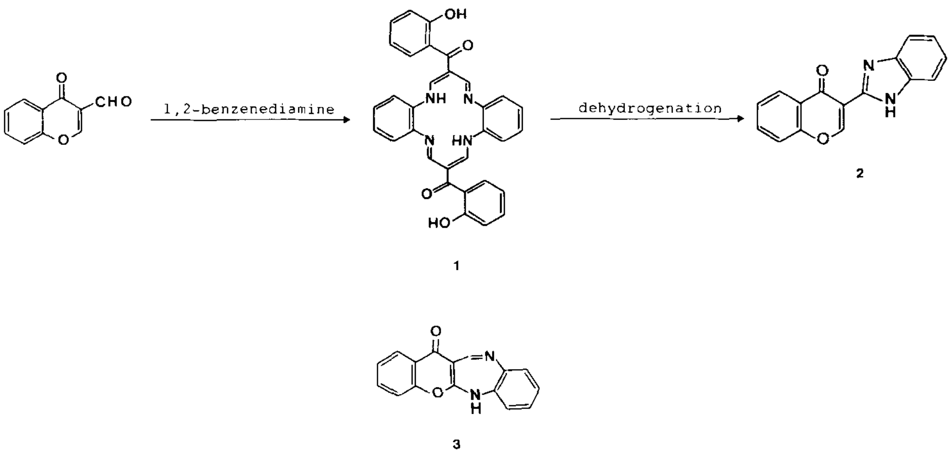
(26.VIII.85)

The reaction product of 4-oxo-4*H*-[1]benzopyran-3-carbaldehyde and 1,2-benzenediamine is 1,8-dihydro-6,13-bis(2-hydroxybenzoyl)dibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (**1**), and its dehydrogenation product is 3-(2-benzimidazolyl)-4*H*-[1]benzopyran-4-one (**2**) as shown by X-ray structure analysis confirming our earlier report.

In 1982, we reported [1] that the reaction product of 4-oxo-4*H*-[1]benzopyran-3-carbaldehyde (3-formylchromone) with 1,2-benzenediamine gives **1** and, on dehydrogenation, **2** at variance with earlier reports [2] *(Scheme)*. Our structure elucidation by NMR methods was met with limited enthusiasm [3]. We, therefore, carried out an X-ray structure analysis of both compounds. The result presented here confirms structures **1** and **2** justifying the NMR methods used previously.

Scheme



The result of the X-ray structure analysis is shown in *Figs. 1* and *2*. Crystal data[1]) for both compounds are given in the *Table*. Intensity measurements were made on a *Philips PW1100* diffractometer with monochromated Mo*Kα* radiation. The structures were solved by direct methods using the computer program MULTAN 78 [5].

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[1]) Atomic coordinates and bond lengths for **1** and **2** are available from the *Crystallographic Data Centre, Cambridge* (UK).

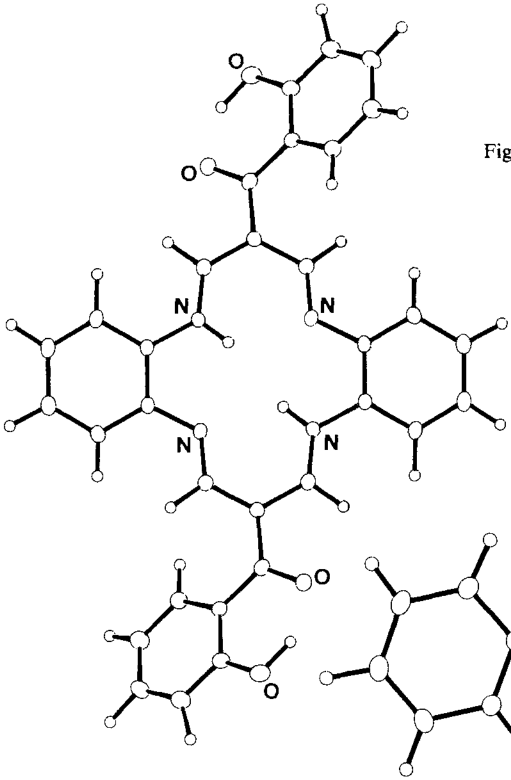

Fig. 1. *ORTEP* [4] *drawing of* **1**

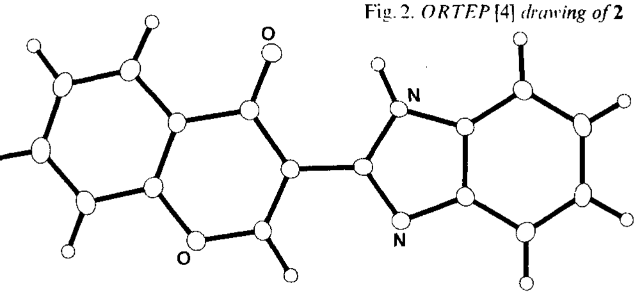

Fig. 2. *ORTEP* [4] *drawing of* **2**

Table. *Crystal Data of* **1** *and* **2**

Compound	**1**	**2**
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbca*
a [Å]	4.302	16.692
b [Å]	25.835	23.617
c [Å]	11.340	6.095
β [°]	101.63	
Z	2	8
Molecular symmetry	C_i	C_1
No. of reflections	1998	1833
No. of parameters	229	221
Final R factor	0.072	0.078

All H-atoms could be located in difference *Fourier* maps. Least-squares refinements were carried out with anisotropic thermal parameters for non-H-atoms and isotropic ones for H-atoms. Final R factors and number of reflections used in the refinements are also listed in the *Table*.

The difference *Fourier* map of **1** showed in the centre of the molecule 4 electron density peaks representing half hydrogen atoms, one associated with each of the N-atoms. There is also an intramolecular H-bond between the O of the keto group and the O of the OH group with an O · · · H distance of 1.58 Å and an O · · · O distance of 2.523 Å. The keto group forms an angle of 27° with the macrocycle and of 15° with the *o*-hydroxyphenyl ring.

Compound **2** is planar within 0.07 Å. There is a weak intramolecular N-H · · · O H-bond with an N · · · O distance of 2.790 Å and a rather large H · · · O distance of 2.16 Å.

The reaction mechanism of the formation of **1** and **2** has already been discussed [1]. The formation of **1** is not surprising, as 3-formylchromone is structurally similar to 3-alkoxy acroleines, which are known to react with aromatic and heterocyclic 1,2-diamines to give tetraaza[14]annulenes [6].

The seven-membered ring structure **3** which was assigned erroneously to compound **2** [2] has been used as reference for the structure assignment of related reaction products in later publications [7]. Without rigorous proof of structure by X-ray or NMR analysis, these structural assignments remain in doubt.

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