

Preparation and Characterization of 8,13-Dioxodinaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamides

Lester Weinberger, Phyllis Unger and Paul Cherin

Research Laboratories, Xerox Corporation, Rochester, New York

Dedicated to Professor Allan R. Day

Research groups in our laboratories have been interested in polymorphism in organic pigments and its influence on photoconductive properties. During this investigation several new pigments were synthesized. These yellow pigments belong to the class of *N*-substituted 8,13-dioxodinaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamides of the formulas shown in Fig. 1. In this paper we describe the

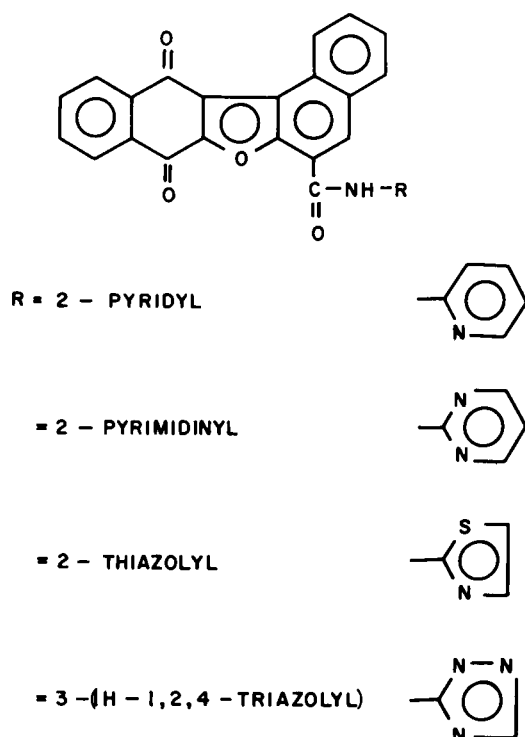
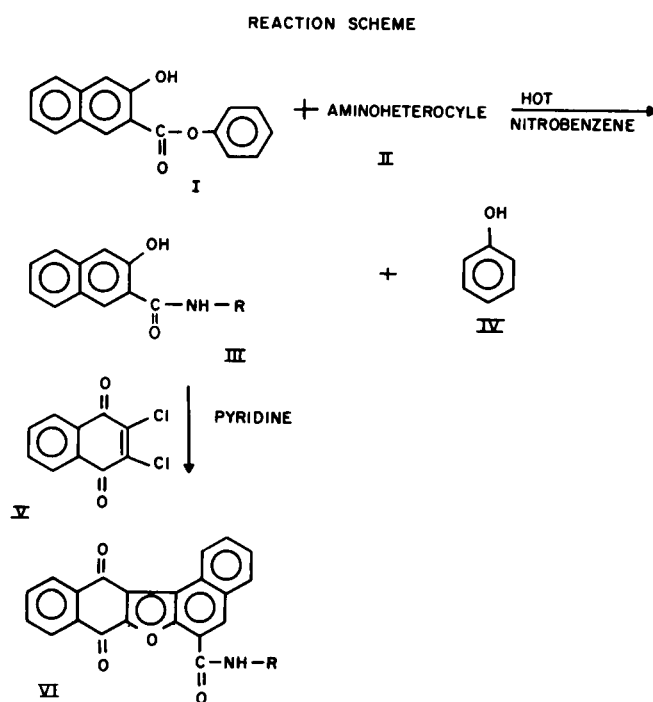


Figure 1

general synthesis of these new pigments and present the unit cell dimensions, space group and lattice spacings of one of the pigments. The lattice spacings are given in Table I.

The general synthesis and the source of the starting materials used is shown in the reaction scheme. In general, phenyl 3-hydroxy-2-naphthoate underwent aminolysis with an aminoheterocycle to form phenol and the corresponding naphthamide; the naphthamide was allowed to react with



I. Phenyl 3-hydroxy-2-naphthoate (Aldrich Chemical Co.)

V. 2,3-Dichloro-1,4-naphthoquinone (Eastman Kodak)

Aminoheterocycles used were:

2-Aminopyridine (Eastman Kodak)

2-aminopyrimidine (Aldrich Chemical Co.)

2-Aminothiazole (Eastman Kodak Practical)

3-Amino-1H-1,2,4-triazole (Eastman Kodak Practical)

2,3-dichloro-1,4-naphthoquinone in the presence of an organic base, pyridine, to yield the fused 5-membered ring system containing the furan nucleus.

In order to investigate polymorphism in these compounds, each pigment was recrystallized from different solvents and studied by X-ray diffractometry. To further characterize each pigment, attempts were made to grow single crystals. To date, suitable single crystals have been obtained only for *N*-2''-pyridyl-8,13-dioxodinaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamide. The best single crystals were grown from warm α -methyl-naphthalene solutions. A crystal in the form of a rectangular parallelepiped with dimensions of approximately 1/2 x 1/3 x 1/4 mm was selected. Single crystal X-ray photographs showed no

TABLE I
Observed and Calculated Lattice Spacings
and Relative Intensities

H	K	L	d_{obs} (Å)	d_{cal} (Å)	I/I_1
1	0	0	19.3	19.5	4
0	1	0	12.99	13.06	2
1	1	0	10.82	10.81	90
2	0	0	9.74	9.73	100
0	1	-1	7.25	7.24	30
2	1	-1	6.52	6.52	50
0	2	-1	6.00	6.02	30
3	-1	0	5.82	5.83	80
3	1	-1	5.46	5.45	25
0	1	1	5.18	5.18	15
4	0	0	4.87	4.87	10
4	-1	0	4.57	4.57	60
0	3	0	4.35	4.35	10
1	-3	0	4.27	4.26	10
3	-2	1	4.07	4.07	5
0	2	1	3.95	3.96	5
4	2	0	3.89	3.89	15
1	2	1	3.79	3.79	10
0	2	-2	3.619	3.618	20
1	0	-2	3.418	3.417	5
0	0	2	3.346	3.347	90
4	3	0	3.233	3.234	5
2	-1	2	3.167	3.163	4
0	3	1	3.125	3.127	4

systematic absences, nor any symmetry other than $I(hk\ell) = I(\bar{h}\bar{k}\bar{\ell})$. Therefore, the space group is either $P1$ or $P\bar{1}$. The absence of a piezoelectric signal suggested $P\bar{1}$ may be the correct space group. Approximate lattice dimensions were determined from the single crystal photographs and subsequently refined using polycrystalline data using a diffractometer. A least squares method developed by one of the authors (1) was used to refine the lattice parameters. The resulting unit cell dimensions are as follows:

$$a = 19.95 \pm .01\text{Å} \quad b = 14.28 \pm .02\text{Å} \quad c = 7.474 \pm .008\text{Å}$$

$$\alpha = 113.80 \pm .05^\circ \quad \beta = 102.66 \pm .05^\circ \quad \gamma = 85.28 \pm .05^\circ$$

The volume is 1901Å^3 . The number of molecules in the unit cell is 4. Both the observed density and the X-ray density are 1.46 g/cm^3 . This indicates that the molecular weight determination is correct. The observed and calculated lattice spacings are compared in Table I. Other crystals gave similar dimensions. Thus far, no evidence for polymorphism has been observed for this system.

Infrared measurements (Table IV) show no indication of dimerization or hydrogen bonding. Thus, none of the

molecules in the unit cell, including those unrelated by symmetry, are bound by any forces stronger than van der Waals.

When suitable single crystals of the other compounds can be grown, they will be similarly characterized and reported at a later date. These compounds also showed no evidence of polymorphism.

TABLE IV

Infrared Spectra cm^{-1}

R	NH Stretch	C=O Stretch
2-Pyridyl	3406 Sharp	1667.0 doublet 1675.5
2-Pyrimidinyl	3415 Sharp	1675; 1700 shoulder, 1705
2-Thiazolyl	3398 Sharp	1670 shoulder; 1675
3-(1H-1,2,4-Triazolyl)	3240 Broad	1675 Broad

EXPERIMENTAL

Melting points were taken with a corrected thermometer in a Hoover melting point apparatus. Density measurements were made on a Beckman air comparison pycnometer Model 930. Infrared spectra were measured with a Beckman IR10 instrument in Nujol mull. Elemental analyses were carried out by Galbraith Laboratories.

Synthesis.

2-N-substituted-3-hydroxynaphthamides (III).

Phenyl 2-hydroxy-3-naphthoate (26.5 g., 0.1 mole) and 0.1 mole of the aminoheterocycle were refluxed in 200 ml. of nitrobenzene for 1 hour. The solution was chilled to 10° and the product was collected by filtration, washed with ethanol and acetone, then dried.

8,13-Dioxodinaphtho[2,1-b:2',3'-d]furan-6-carboxamides (VI).

A mixture of 11.35 g. (0.05 mole) of 2,3-dichloro-1,4-naphthoquinone (V), and 0.05 mole of a 2-N-substituted-3-hydroxynaphthamide (III) was refluxed for 1 hour in 100 ml. of pyridine. The solution was cooled; the crystals were removed by filtration, washed with ethanol and acetone, then dried. The products were recrystallized. For additional information concerning the 8,13-dioxodinaphtho[2,1-b:2',3'-d]furan-6-carboxamides (VI) and the intermediates, 2-substituted-3-hydroxynaphthamides, see Tables II and III, respectively. A similar product has been prepared previously (2) using aniline as the starting material.

X-Ray Measurements.

A rectangular, parallelepiped-shaped crystal was mounted with Duco $\text{\textcircled{R}}$ cement on a glass fiber. Zero (hk0) and first (hk1) layer Weissenberg photographs were taken; precession photographs of the hk0, h0 ℓ and 0k ℓ zones were taken; $\text{CuK}\alpha$ (Ni-filtered) radiation was used. A diffractometer trace of a polycrystalline sample was obtained on a Phillips Electronics unit using $\text{CuK}\alpha$ (monochro-

TABLE II

N-Substituted-8,13-dioxodinaaphtho[2,1-b:2',3'-d]furan-6-carboxamides

R	Recrystallizing Solvent	Yield %	M.P. °C(dec.)	Formula	Carbon		Hydrogen		Nitrogen		Sulfur	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Pyridyl	α -methyl naphthalene	21.6	334	C ₂₆ H ₁₄ N ₂ O ₄	74.63	74.87	3.37	3.57	6.69	6.66		
2-Pyrimidinyl	DMF	63.2	334-334.5	C ₂₅ H ₁₃ N ₃ O ₄	71.60	71.12	3.12	3.39	10.01	9.65		
2-Thiazolyl	DMF	22.2	356-358	C ₂₄ H ₁₂ N ₂ O ₄ S	67.91	67.99	2.85	3.40	6.59	6.95	7.54	7.63
3-(1H-1,2,4-Triazolyl)	α -methyl naphthalene	13.9	405-407	C ₂₃ H ₁₂ N ₄ O ₄	67.64	67.69	2.96	3.44	13.69	13.59		

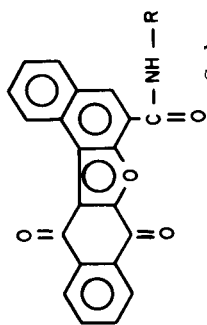
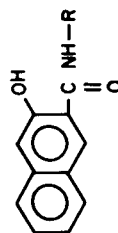


TABLE III

2-N-Substituted-3-hydroxynaphthamides

R	Yield %	M.P. °C(dec.)	Formula	Carbon		Hydrogen		Nitrogen		Sulfur	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Pyridyl	91.0	262-263	C ₁₆ H ₁₂ N ₂ O ₂	72.71	72.21	4.58	4.65	10.57	10.37		
2-Pyrimidinyl	17.8	290-292	C ₁₅ H ₁₁ N ₃ O ₂	67.92	67.70	4.18	4.30	15.84	15.64		
2-Thiazolyl	72.0	302-304	C ₁₄ H ₁₀ N ₂ O ₂ S	62.21	62.01	3.73	3.55	10.36	10.17	11.86	12.01
3-(1H-1,2,4-Triazolyl)	72.8	357-359	C ₁₃ H ₁₀ N ₄ O ₂	61.41	61.61	3.96	4.01	22.04	21.87		



matic) radiation. The lattice spacings in Table I were taken from this trace. The relative intensities were normalized with respect to the peak height of the (200) reflection.

Acknowledgement.

The authors are pleased to acknowledge the help of P. Cressman, G. Faucz, G. Fekete and H. Six.

REFERENCES

- (1) P. Cherin and P. Unger, "Polymorphic Forms of Phthalocyanine," National Meeting of the American Chemical Society, Chicago, Sept., 1967.
- (2) B. Suryanarayana and B. D. Tilak, *Proc. Indian Acad. Sci., Sect. A*, 37, 81 (1953).

Received June 14, 1969

Rochester, New York 14603