

crystals will grow as the solvent evaporates. Fragments of cover glass or of seed crystals should be present under the cover glass in order to obtain crystals thick enough to give distinct interference figures. The immersion oils used for refractive index measurements were removed by flooding repeatedly with petroleum ether or isooctane.

The angular measurements shown in Fig. 2 were made on crystals grown from aqueous solution. Refractive indices were measured on crystals from both sources. The fact that this compound is optically active requires that the crystals be hemimorphic although no forms (that would require this classification) were seen.

*Crystal System:* Monoclinic, Beta Angle = 107°.

*Optical Properties:* Refractive Indices (5893A; 27°)  $\alpha = 1.520$ ,  $\beta = 1.530$ ,  $\alpha\gamma = 1.534$ ,  $\beta'$  and  $\beta'' = 1.532$  (Fig. 2).

*Optic Axial Angle* (5893A; 27°)  $2E = 65^\circ$ .

*Dispersion:* Not noticeable.

*Optical Character:* Negative.

*Acute Bisectrix:*  $\alpha = b$ .

*Extinction:* Views having b vertical show oblique extinction with the vibration direction  $\beta$  making an angle of 34° with the length direction (Fig. 2). Such views are rare. They show a hazy acute bisectrix interference figure. The most common view is that of a crystal lying on one of its main faces (110). Such a view which exhibits sweeping extinction, does not show any principal optical direction but exhibits a refractive index for nearly lengthwise vibrations of 1.532. The interference figure for this view shows one optic axis near the edge of the aperture (N.A. = 0.95). Crystals that have the greatest retardation and sharp parallel or symmetrical extinction lie on either (100) or (001). Such views show  $\alpha$  crosswise and  $\beta''$  or  $\beta'$ , respectively. The interference figure is symmetrical but centered between the obtuse bisectrix and the optic normal.

*Fusion Data:* Crystals melt without noticeable decomposition but no crystals grow in the viscous melt which cools to a glass.

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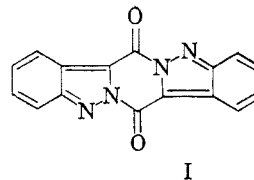
## Diindazolo[2,3-*a*, 2',3'-*d*]pyrazine-7,14-dione

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In the course of preparing some 3-indazolecarboxylic acid derivatives we attempted the preparation of 3-indazolecarbonyl chloride by the action of thionyl chloride on 3-indazolecarboxylic acid. The acid chloride had been reported but not characterized by previous workers.<sup>1</sup> Isolation of the "acid chloride" gave an orange-red compound containing no chlorine. Elemental analyses and saponification equivalent led to the consideration of I as the most likely structure.

(1) H. R. Snyder, C. B. Thompson, and R. L. Hinman, *J. Am. Chem. Soc.*, **74**, 2009 (1952).



I

A search of the literature revealed that von Auwers and Cauer<sup>2</sup> indicated the preparation of I but gave no physical constants or analytical data. However in a later paper von Auwers and Wolter<sup>3</sup> reported the preparation of the 1,2,3,4,8,9,10,11-octahydro derivative of I from the corresponding tetrahydroindazolecarboxylic acid and gave a structure analogous to I.

In common with other workers<sup>4</sup> using diketopiperazine derivatives derived from various 3-pyrazolecarboxylic acids, I was found to be an active acylating agent. On treatment with aqueous dimethylamine, an 85% yield of *N,N*-dimethyl-3-indazolecarboxylic acid amide<sup>1</sup> was obtained.

The formation of a polycyclic compound in the benzimidazole group has been reported.<sup>5</sup> The action of thionyl chloride on benzimidazole-2-acetic acid gave a compound whose structure is similar to I and which also readily acylates amines.

### EXPERIMENTAL<sup>6</sup>

*Diindazolo[2,3-*a*, 2',3'-*d*]pyrazine-7,14-dione (I).* A slurry of 53 g. of 3-indazolecarboxylic acid<sup>1</sup> and 100 cc. of thionyl chloride was heated under reflux for 2 hr. A large volume of benzene was added and the product filtered. The reddish-orange solid was suspended in Skelly E and heated on the steam bath to expel thionyl chloride. The product was filtered, washed with pentane, and dried. The yield was 30.0 g. (64%), m.p. >350°. The product was found to be insoluble in common organic solvents and was purified by extraction with boiling acetone for 3 hr. The insoluble orange solid gave the following results.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>: C, 66.66; H, 2.80; N, 19.44; sapon. equiv. 144. Found: C, 66.49; H, 3.24; N, 19.45; sapon. equiv. 144.

*N,N*-Dimethyl-3-indazolecarboxylic Acid Amide. The diamide I (30 g.) was treated with 200 cc. of 25% aqueous dimethylamine. A mild exothermic reaction resulted and the reaction mixture was allowed to stand overnight at room temperature. The product was isolated by heating on the steam bath to drive off dimethylamine, followed by cooling and filtration. The dried white solid weighed 33.4 g. (85%), m.p. 191–193° (uncorr.). Recrystallization from nitromethane did not alter the melting point. (The reported<sup>1</sup> m.p. is 187–189°).

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O: N, 22.21. Found: N, 21.97.

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- (2) K. von Auwers and E. Cauer, *Ber.*, **61**, 2402 (1928).
- (3) K. von Auwers and E. Wolter, *Ber.*, **63**, 479 (1930).
- (4) C. Musante and P. Pino, *Gazz. chim. ital.*, **77**, 199 (1947).
- (5) R. A. B. Copeland and A. R. Day, *J. Am. Chem. Soc.*, **65**, 1072 (1943).
- (6) Analyses are by Messrs. M. E. Auerbach, K. D. Fleischer, and their staffs.