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1. The literature is summarised by Lindgren, B. O. *Svensk Papperstidn.* **55** (1952) 78.
2. Lindgren, B. O. *Acta Chem. Scand.* **5** (1951) 603.
3. Enkvist, T., and Moilanen, M. See reference 1.
4. Adler, E., and Yllner, S. *Svensk Papperstidn.* **55** (1952) 238.
5. Adler, E., Lindgren, B. O., and Saedén, U. *Svensk Papperstidn.* **55** (1952) 245.
6. Tipson, R. S., and Cretcher, L. H. *J. Org. Chem.* **8** (1943) 95.
7. Hann, R. M., Ness, A. T., and Hudson, C. S. *J. Am. Chem. Soc.* **66** (1944) 73.
8. Tipson, R. S., Clapp, M. A., and Cretcher, L. H. *J. Org. Chem.* **12** (1947) 133.
9. Karrer, P., Schick, E., and Schwyzer, R. *Helv. Chim. Acta.* **31** (1948) 784.
10. Lindstedt, G. *Arkiv Kemi Mineral. Geol.* **A 20** (1945) no. 13.
11. Erdtman, H. *Svensk Papperstidn.* **48** (1945) 75.

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A Preliminary X-Ray Investigation of Dipicrylamine and some of Its Salts

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The potassium salt of dipicrylamine, or 2,4,6-2',4',6'-hexanitrodiphenylamine, is almost insoluble in water, and it has been proposed to make use of this to manufacture potassium from sea-water¹. The salt exists in at least two polymorphic forms, one red and one violet. These are distinguished by their different reactivity towards nitric acid, which is used to regenerate the amine from the salt². It was therefore thought to be of interest to investigate the crystal structure of the two polymorphic forms. Besides, the dipicrylamine molecule presents in itself interesting stereochemical problems.

We have studied a number of dipicrylamines by X-ray methods in order to find a compound suitable for complete structure determination. Single crystals of the substances were prepared by dissolving the calcium salt in water and precipitating the alkaline salts by adding the corresponding cations. The red form of the potassium salt was obtained by evaporating an aqueous solution of the salt at room temperature, the violet form by evaporation at 70° C². X-ray oscillation and Weissenberg diagrams were taken, using CuK α and FeK α radiation (wave lengths 1.542 Å and 1.937 Å resp.), and the densities measured by the flotation method. The results are believed to be correct to about 1 %.

In the following the results of the measurements are given, the dipicrylamine anion being called *D* for short.

HD (dipicrylamine). The yellow, well-developed crystals have the shape of short prisms elongated parallel to *a*. Forms {010}, {210}, and {011} were observed. The crystals are orthorhombic, with cell dimensions *a* = 18.94 Å, *b* = 11.72 Å, and *c* = 7.37 Å. Reflexions *h*00, 0*k*0 and 00*l* are absent for *h*, *k* and *l* odd respectively and as no other systematic absences occur, the space group is *P*₂₁²₁²₁. The density was found to be 1.77 g/cm³ and there are four (calc. 3.97) molecules in the unit cell.

After this investigation was completed, McCrone³ has published crystal data on HD. His findings are in agreement with the measurements reported above (*a* = 11.75 Å, *b* = 19.10 Å, *c* = 7.43 Å; density 1.750 g/cm³; space group not given).

NaD. Red orthorhombic plates {001}, with *a* = 17.61 Å, *b* = 11.77 Å, and *c* = 7.86 Å. Density 1.89 g/cm³ four (calc. 4.02) mols. in the unit cell. Space group *P*₂₁²₁²₁.

KD, red form. Thick, rhombic plates, bounded by {11*l*} and {001}, the latter form predominant. The *b* axis bisects the oblique angle. The crystals are monoclinic, with *a* = 15.77 Å, *b* = 13.00 Å, *c* = 11.02 Å, and β = 130°. Density 1.84

g/cm³; four (calc. 4.03) mols. in the unit cell. The only systematic absences occur in the $h0l$ reflexions for h odd and in the $0k0$ reflexions for k odd, and the space group is therefore $P2_1/a$.

KD, violet form. Plates $\{100\}$, elongated along the c axis. Monoclinic, with $a = 15.12$ Å, $b = 13.70$ Å, $c = 9.15$ Å, and $\beta = 115^\circ$. Density 1.84 g/cm³; four (calc. 4.00) mols. in the unit cell. Systematic absences and space group as for the red form, $P2_1/a$.

RbD. The crystals have the same shape as those of the red form of KD. They are monoclinic, with $a = 15.97$ Å, $b = 13.22$ Å, $c = 11.02$ Å, and $\beta = 130^\circ$. Density 1.96 g/cm³; four (calc. 4.03) mols. in the unit cell. The space group is $P2_1/a$. The $00l$ reflexions are very weak for odd values of l .

CsD. Monoclinic plates $\{001\}$, with $a = 13.90$ Å, $b = 10.64$ Å, $c = 11.54$ Å and $\beta = 92^\circ$. Density 2.25 g/cm³; four (calc. 4.05) mols. in the unit cell. The hkl reflexions are absent for $h + k$ odd, and the $h0l$ reflexions for l odd. Possible space groups are $C2/c$ and Cc , the latter being the most likely one, as the molecule probably is asymmetrical.

Discussion of results. It will be seen that the red and violet forms of KD have the same space groups and fairly similar unit cell dimensions. The development of crystal faces is, however, quite different in the two cases, as $\{001\}$ is predominant in the red form and $\{100\}$ in the violet form. This may possibly be connected with the difference in reactivity of the two forms towards nitric acid. Red KD is isomorphous with RbD. An attempt was made to solve the structure of the latter by Patterson and Fourier projections along the b axis. The vector map indicated $x = 0.10$ and $z = 0.24$ as possible co-ordinates for the Rb atom, but we did not succeed in interpreting the corresponding Fourier map.

Grison⁴ has determined the structure of three polymorphic forms of *N*-picryl-*p*-

iodoaniline, a compound which differs from HD in having no nitro groups in one of the benzene rings. Grison finds that the angle C-N-C at the amino-nitrogen is 138° and that the two benzene rings are rotated relative to one another through 65° . It appears likely that the corresponding angles in the dipicrylamine molecule are of the same order of magnitude, as it can be shown by means of a model that the introduction of nitro groups also in the other benzene ring may be compensated by suitable rotation of the ortho nitro groups.

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1. Kielland, J. Norwegian Pat. 62187 (1938), 64237 (1939) and 63072 (1941).
2. Kielland, J. Private communication.
3. McCrone, W. C. *Analyt. Chem.* **24** (1952) 592.
4. Grison, E. *Acta Cryst.* **2** (1949) 410.

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Polymorphism and Thermal Instability of 1 κ , 2 κ , 4 κ , 5 κ -Tetrabromocyclohexane

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Recently 1 κ , 2 κ , 4 κ , 5 κ -tetrachlorocyclohexane (m.p. 226°C) and 1 κ , 2 κ -dichloro-4 κ , 5 κ -dibromocyclohexane (m.p. 240°C) have been prepared¹. It was shown that both substances are dimorphous, corresponding modifications being isomorphous. The transition temperatures are $60-65^\circ\text{C}$ and $90-95^\circ\text{C}$ respectively. The tetrachloro-compound is stable above the melting point, but the dichloro-dibromo-compound, when heated above the melting point is transformed — at least to a large extent — into the stereoisomer of m.p. 171°