

## A Correction of the Crystal Structure of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$

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In order to refine the crystal structure of  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$  a reinvestigation was started in this Institute. Prolonged exposures then showed that the crystal has a considerable superstructure. The new axes  $a, b, c$  are related to the earlier  $a', b', c'$  in the following way:  $a = 4a', b = 2b', c = 2c'$ . The cell dimensions are thus  $a = 15.08 \text{ \AA}, b = 13.82 \text{ \AA}, c = 14.68 \text{ \AA}$  and  $\beta = 90^\circ 40'$ . The loss of orthorhombic symmetry which could not be detected in the intensities earlier is now obvious for the superstructure reflexions. It has been checked that the main principles of the suggested structure cannot be influenced by the superstructure but there are of course, small changes in the oxygen positions. The calculated bond distances (except for Mo-Mo) are thus of little value and therefore the basis is removed for the suggestion about the existence of an ion  $\text{H}_4\text{O}^{2+}$ .

Because of change of axes during the work an obvious error has been made in the description of the structure in Ref.<sup>1</sup>:  $x$  and  $z$  parameters and  $h$  and  $l$  indices should be interchanged all through the paper to fit the choice of axes.

A complete reinvestigation will be very time-consuming and is not planned at present.

1. Lindqvist, I. *Acta Chem. Scand.* 4 (1950) 650.

Received October 17, 1956.

## A Nuclear Magnetic Resonance Study of the Dihydrate of Molybdenum Trioxide

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A combined proton magnetic resonance and infra-red investigation of the dihydrate of molybdenum trioxide has shown

that the formula  $(\text{H}_4\text{O}^{2+})\text{MoO}_4^-$  is very improbable<sup>1</sup>.

The second moment of the proton absorption line at  $77^\circ \text{K}$  is 27.6 gauss<sup>2</sup>. If a symmetrical  $\text{H}_4\text{O}^{2+}$  ion existed in the crystal, this value would predict<sup>3</sup> an O-H distance of 1.16 Å in  $\text{H}_4\text{O}^{2+}$ , compared with 0.96 Å in water vapour, and this seems an improbably large increase. In addition, the infra-red spectrum shows frequencies at 3100 and 1592  $\text{cm}^{-1}$ ; if these are interpreted as stretching and bending frequencies associated with O-H groups, they suggest an expansion of the order of 0.04 Å only. It would be difficult to reconcile both of these results with the existence of an  $\text{H}_4\text{O}^{2+}$  ion.

We hope to publish these results in detail elsewhere.

1. Lindqvist, I. *Acta Chem. Scand.* 4 (1950) 650.
2. Van Vleck, *Phys. Rev.* 74 (1948) 1168.

Received October 17, 1956.

## Metalation of Pyrene

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Only few strictly aromatic hydrocarbons have been metalated by organolithium compounds<sup>1</sup> and the yields of carboxylic acids obtained upon carbonation have been poor.

Pyrene, in view of its readiness to partake in substitution reactions, and especially of the general rule of substitution in 3-position<sup>2</sup> governing these reactions, seemed an interesting object for metalation.

It has now been found that pyrene, by the action at room temperature of a rather large excess of *n*-butyllithium in diethyl ether not only is metalated as evidenced by the isolation of pyrene carboxylic acids upon carbonation of the reaction mixture, but also is attacked by the organometallic reagent in positions 1 and 4 in addition to the usual 3-position, that is in all isomeric positions in the pyrene molecule. This was shown by the isolation from the acid mixture of three acids two of which were

*Acta Chem. Scand.* 10 (1956) No. 8

identical with the known pyrene-3- and pyrene-4-carboxylic acids. The third acid, also being, as shown by analysis, a pyrene-monocarboxylic acid, consequently must be the hitherto unknown pyrene-1-carboxylic acid<sup>2</sup>. Its constitution has been further established by converting it to the known 1-methyl-pyrene *via* 1-pyrenyl carbinol by reduction with lithium aluminium hydride. Also the carbinol is new. The 3-acid itself appeared difficult to isolate in a pure state, but it could be identified as the methyl ester.

The isomer ratio, as roughly estimated from the yields of the three acids in an experiment as described below, was 2:1:0.2, the positions taken in the order 1, 3 and 4. In a typical experiment a conversion of 85 % of pyrene was found, the remainder being recovered. Of converted pyrene 70 % were isolated as acidic products, 70 % of which consisted of the three pyrene-monocarboxylic acids.

More details will appear in a following paper and the present work is continued in different directions.

*Experimental.* Pyrene (20 g; 0.1 mole) in absolute ether (300 ml) was treated with a filtered solution of *n*-butyllithium, prepared, according to Gilman *et al.*<sup>3</sup>, from lithium (8.5 g; 1.22 g. atoms) and *n*-butyl bromide (68.5 g; 0.5 mole) in abs. ether (200 ml). The colour of the solution rapidly turned deep red. After 14 days the solution was pressed into a mixture of dry ice and ether and worked up. From the ether layer pyrene (3.1 g) was recovered. The acidic products were separated by fractionated salting out of the sodium salts. In this way and by recrystallization from acetic acid and chlorobenzene more or less pure fractions of the three pyrene-monocarboxylic acids resulted, amounting to 10.2 g. By repeated recrystallizations pure fractions of the 1- and 4-acids were obtained. The last named acid (m.p. 327—328°) as well as the methyl ester (m.p. 139°; esterification was accomplished with methanolic hydrogen chloride) did not show any depression in mixed m.p. with authentic samples. Not quite pure 3-acid (m.p. about 260°; the pure acid has m.p. 273°) was esterified with methanol and hydrogen chloride and the crude methyl ester chromatographed (in benzene-hexane, 1:1) on alumina. The bulk of the ester was obtained with m.p. 82° and did not show any depression in mixed m.p. with authentic 3-ester (m.p. 83—84°).

*Pyrene-1-carboxylic acid.* Light yellow fractions with sharp m.p. 275—276° were obtained from chlorobenzene (Found: Equiv. wt. by titration 246.6; C 83.16; H 4.27. Calc. for C<sub>17</sub>H<sub>10</sub>O<sub>2</sub>: Equiv.wt. 246.3; C 82.90; H 4.09). The 1-acid dissolves in conc. sulphuric acid with a yellow colour but without fluorescence (the 3-acid shows a strong yellow-green fluorescence). Esterification in methanolic hydrogen chloride yielded the methyl ester of the 1-acid, m.p. 107—108° (from methanol) (Found: C 83.14; H 4.79. Calc. for C<sub>18</sub>H<sub>12</sub>O<sub>2</sub> (260.3): C 83.05; H 4.65). Ultraviolet absorption maxima of the ester (in ethanol) were found at: 218.5, 240.4, 253, 280, 310.5, 341.5 and 380.5 m $\mu$ .

*1-Pyrenyl carbinol.* Pyrene-1-carboxylic acid (0.93 g) was extracted down into a stirred suspension of lithium aluminium hydride (0.5 g) in ether in the course of 4 h and the mixture refluxed for an additional hour before it was hydrolyzed and worked up. The organic layer by evaporation of the ether left the carbinol as thin, white needles. Recrystallization from benzene yielded 0.82 g with m.p. 155—155.5° (Found: C 87.50; H 5.18. Calc. for C<sub>17</sub>H<sub>12</sub>O (232.3): C 87.88; H 5.21). Ultraviolet absorption maxima were found at 233, 242, 253.5, 264, 274.5, 307.5, 321, 336.7, 351, 363.5 and 373.5 m $\mu$  (in ethanol).

The 1-carbinol (0.5 g) was converted to the corresponding chloride as described by Bachmann and Carmack<sup>4</sup> for the 3-carbinol and the chloride then reduced with lithium aluminium hydride in boiling ether. After hydrolysis only a minor part could be identified as definite compounds. The crude product was fractionated from ethanol, and fractions showing a green fluorescence with conc. sulphuric acid (the carbinol does not show this) were chromatographed on alumina (from benzene-hexane, 1:1), when small amounts of 1-pyrenyl carbinol (25 mg) and of not quite pure 1-methyl-pyrene (50 mg) could be isolated. After recrystallization from ethanol the 1-methyl-pyrene fraction (30 mg) showed m.p. 144.5—145°. Repetition of the whole purification procedure brought the m.p. to 147.5—148°. There was no m.p. depression with an authentic specimen of 1-methyl-pyrene whereas a specimen of 4-methyl-pyrene (m.p. 145—146°) depressed the m.p. drastically. The two authentic methyl pyrenes were very kindly supplied by Dr. H. Dannenberg, Max-Planck Institute in Munich and by Dr. O. Kruber, the Gesellschaft für Teerverwertung, Duisberg-Meiderich, to whom I am very much indebted. Also the m.p. of the picrate (228—229°, from

benzene) as well as the ultraviolet absorption spectrum of the hydrocarbon itself agreed with 1-methylpyrene.

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2. Vollmann, H., Becker, H., Correll, M. and Streeck, H. *Ann.* **531** (1937) 73.
3. Gilman, H., Beel, J. A., Brannen, C. G., Bulluck, M. V., Dunn, G. E. and Miller, L. S. *J. Am. Chem. Soc.* **71** (1949) 1499.
4. Bachmann, W. E. and Carmack, M. J. *Am. Chem. Soc.* **63** (1941) 2494.
5. Added in proof: Recently a paper by O. Neunhoeffer and H. Woggon [*Ann.* **600** (1956) 34] appeared reporting the formation of pyrene-1-carboxylic acid (m. p. 258° is reported) by the action of metallic sodium on pyrene followed by carbonation. The metalorganic intermediate is shown to be an addition product of 1 sodium atom with 1 molecule of pyrene.

Received October 17, 1956.