

situated at 44 000 and 49 000  $\text{cm}^{-1}$  in the free ions <sup>4</sup>, the crystal field splittings of the excited terms must here be considerable in order to explain the low wavenumbers observed. It might be argued that <sup>7</sup>S of 3d<sup>5</sup>4s in Fe<sup>2+</sup> at 30 000  $\text{cm}^{-1}$  should give even lower wavenumbers. But for more than five d-electrons, the highest multiplicity of 3d<sup>n-1</sup>4s gives spin-forbidden bands, and first <sup>5</sup>S at 41 000 and <sup>6</sup>G at 63 000  $\text{cm}^{-1}$  will give ordinary intensities in Fe<sup>2+</sup>, where a band<sup>12</sup> is observed  $\sim 40\,000\text{ cm}^{-1}$ .

Orgel<sup>2</sup> and Owen<sup>3</sup> investigate the possibility of covalent bonding, *i. e.* molecular orbitals being occupied by electrons from both central ion and ligands. This is undoubtedly the case of ligands with considerable electron affinity, as CO, CN<sup>-</sup>, NO<sup>+</sup>, aromatic amines, PCl<sub>3</sub>, trialkylphosphines, but it is not easily decided in the case of ordinary ligands (H<sub>2</sub>O, NH<sub>3</sub>, *etc.*) where the most conspicuous effect<sup>2,3</sup> on the absorption spectra is only an increased energy difference ( $E_1 - E_2$ ) between  $\gamma_3$ - and  $\gamma_5$ -electrons, analogous to the crystal field influence. It is interesting that ( $E_1 - E_2$ ) is nearly constant  $\sim 20\,000\text{ cm}^{-1}$  in trivalent hexaquo ions, while it is  $\sim 10\,000\text{ cm}^{-1}$  in divalent ions, and here decreasing<sup>1</sup> with the atomic number as implied from the theory<sup>13</sup>. This can only be explained by considerably smaller distances to the effective negative charges of the ligands of the trivalent ions than in the divalent ions, if the covalent hypothesis is not accepted. It must be remarked that the parameters in the crystal field model of Ilse and Hartmann<sup>13</sup> have no quantitative physical significance. *E. g.*, the hydrogen-like 3d wavefunction with the effective charge  $Z = 4$  has its maximum at a distance 1.18 Å from the nucleus, while the radius of Ti<sup>3+</sup> is assumed to be 0.8 Å. Some problems related to effective quantum numbers will be discussed elsewhere<sup>14</sup>. The transitions between different configurations, 5f<sup>n</sup>  $\rightarrow$  5f<sup>n-1</sup>6d in the actinide ions, are also known from absorption spectra<sup>15</sup>.

A valuable implication from the theory of molecular orbitals<sup>2,3</sup> is that the strong electron transfer bands are due to transitions from the odd  $\gamma_4$ -states. Hartmann<sup>16</sup> pointed out that the series of energy of the molecular orbitals in an octahedral complex should be:

$$\gamma_1, \gamma_4, \gamma_3, \gamma_5(d), \gamma_3(d), \gamma_1(s), \gamma_4(p) \dots$$

If the lowest  $\gamma_3$  had a much higher energy than the lowest  $\gamma_4$ , weak bands would be

found in the electron transfer spectra at lower wavenumbers than the strong bands.

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## Dihydro-thionaphthene-2- and -3-carboxylic Acids

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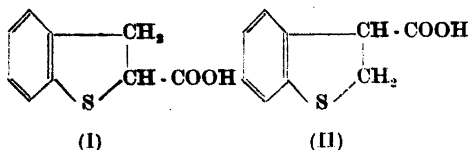
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The acids have been prepared in connection with current work on optically active plant growth substances. They are easily obtained by hydrogenation of the corresponding thionaphthene-carboxylic acids using sodium amalgam.

The biological properties are being investigated by several scientists. The 3-acid (II) possesses auxin activity while the 2-acid (I) seems to be an anti-auxin.

The 2-acid is readily resolved into the enantiomorphs using brucine and cinchonine. The rotatory power is rather high (ca. 365° in absolute ethanol); this is no doubt due to the cyclic structure and the presence of a sulphur atom linked to the asymmetric carbon. The resolution will be described in detail elsewhere.

The alkaloid salts of the 3-acid have a rather low tendency to crystallise and the resolution of this acid has not yet been completed.



**Experimental.** *Dihydro-thionaphthene-2-carboxylic acid (I).* The corresponding thionaphthene-2-carboxylic acid was prepared by metalation of thionaphthene with *n*-butyllithium and subsequent treatment with carbon dioxide; the method was given by Shirley and Cameron<sup>1</sup> and independently by Gronowitz<sup>2</sup>.

Sodium hydroxide (25 g) was dissolved in 400 ml water and 18.0 g (0.1 mole) thionaphthene-2-carboxylic acid was added. A sparingly soluble sodium salt separated. Sodium amalgam, prepared from 6.5 g sodium and 260 g mercury, was added with stirring during 20 minutes. As the sodium salt of the dihydro acid is readily soluble, the precipitated salt goes into solution as the reaction proceeds; it was completely dissolved after 45 minutes. The solution was stirred for another 45 minutes and left to stand with the amalgam overnight. The mercury was then separated and the solution neutralised and filtered with carbon. The acid was precipitated with sulphuric acid in excess. After drying it was recrystallised four times, alternatingly from dilute formic acid and benzene. Glistening plates or flat needles with m.p. 112–113°. (Found: C 60.01; H 4.48; S 17.70; equiv. wt. 180.4. C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>S requires C 59.98; H 4.47; S 17.78; equiv. wt. 180.2.)

*Dextrorotatory acid.* Racemic acid was converted to brucine salt, which was recrystallised four times from 50% aqueous methanol; the activity remained constant after two recrystal-

lisations. The acid was liberated and recrystallised twice from ligroine (b.p. 85–110°). Plates or flat needles with m.p. 94.5–95°. (Equiv. wt. found 180.5; calc. 180.2.  $[\alpha]_D^{25} = +365.4^\circ$  in absolute ethanol.)

*Levorotatory acid.* The acid liberated from the first mother liquor of the brucine salt was converted to cinchonine salt, which was recrystallised four times from dilute ethanol; the activity remained constant after two recrystallisations. The acid was liberated and recrystallised as described above. Plates or flat needles with m.p. 94.5–95°. (Equiv. wt. found 180.3; calc. 180.2  $[\alpha]_D^{25} = -365.8^\circ$  in absolute ethanol.)

*Dihydro-thionaphthene-3-carboxylic acid (II).* The corresponding thionaphthene-3-carboxylic acid was prepared from 3-bromothionaphthene according to Komppa and Weckman<sup>3</sup>. The yield could be considerably improved by performing the Grignardation in the presence of an equivalent amount (excess not necessary) of ethyl iodide according to Crook and Davies<sup>4</sup>. It is also convenient to dilute the Grignard solution with dry benzene before the treatment with carbon dioxide.

22 g (0.122 mole) thionaphthene-3-carboxylic acid were dissolved in 500 ml 2 *N* sodium hydroxide solution. Sodium amalgam, prepared from 6.5 g sodium and 200 g mercury, was added with stirring in the course of one hour. The stirring was continued for six hours and the solution was left to stand overnight. It could be noticed that the reaction proceeded slower than for the 2-isomeride.

The solution was separated from the mercury, the acid was precipitated with sulphuric acid in excess, decolourised with charcoal and recrystallised from cyclohexane. Long, glistening needles with m.p. 99.5–100.5°. (Found: C 59.83; H 4.40; S 17.77, 17.63; equiv. wt. 180.5. C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>S requires C 59.98; H 4.47; S 17.78; equiv. wt. 180.2.)

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