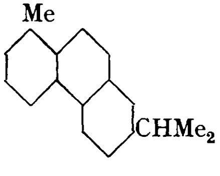
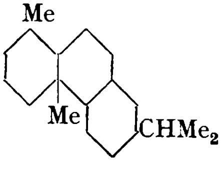
NOTES.

The Molecular Weight of Fichtelite. By DOROTHY CROWFOOT.

FICHTELITE was discovered as colourless crystals in a peat bog by Bromeis (*Ann. Pharm.*, 1841, **37**, 304), who showed that it was a simple hydrocarbon, although he classified it as a mineral or " fossil resin." Its close structural relationship to the terpenes and particularly to abietic acid was suggested by the work of Ruzicka, Balas, and Schinz (*Helv. Chim. Acta*, 1923, **6**, 692), who found that on dehydrogenation with sulphur it was converted into retene. The elementary analysis of fichtelite supports the formula $C_{18}H_{32}$ but does not exclude $C_{19}H_{34}$. In the first case the most probable structure for fichtelite is that of a simple reduced retene derivative (I). In the second, the molecule must contain an angle methyl group, lost on dehydrogenation, and may probably be assigned the structure (II) by analogy with abietic acid. This possibility is supported by the isolation of methane among the dehydrogenation products of fichtelite by Ruzicka and Waldmann (*Helv. Chim. Acta*, 1935, **18**, 611).

(I.)





(II.)

At the suggestion of Dr. Rosenheim I have carried out an *X*-ray examination of crystals of fichtelite (m.p. 46°) kindly given me by Professor Ruzicka. The results of the molecular weight determination exclude the formula $C_{18}H_{32}$, and therefore structure (I), and agree very well with the requirements of structure (II).

The crystals are described by Groth ("Chemische Krystallographie," V, p. 436), who records a number of previous crystallographic examinations. They are monoclinic prisms or thick plates, showing $\{001\}$ dominating and elongated along [010]. The axial ratios are given by Groth as $a : b : c = 1{\cdot}433 : 1 : 1{\cdot}756$; $\beta = 126° 57'$; though Rosati's measurements (*Atti R. Accad. Lincei*, 1911, **20**, II, 212) show that there are small deviations in these constants among crystals obtained from different sources. The plane of the optic axes is (010) with α inclined at about 8° to (001) towards c. The birefringence is negative and the refractive indices have been measured by Plzak and Rosicky (*Z. Krist.*, 1908, **44**, 332) as $\alpha = 1{\cdot}544$, $\beta = 1{\cdot}572$, $\gamma = 1{\cdot}598$. There is a general similarity to certain types of sterol crystal (cf., for example, Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1032) and this is borne out by the unit cell dimensions determined by the *X*-ray method: $a = 10{\cdot}69 \pm 0{\cdot}03$, $b = 7{\cdot}45 \pm 0{\cdot}01$, $c = 13{\cdot}10$ A., $\beta = 127° 5' \pm 5'$, $c \sin \beta = 10{\cdot}45 \pm 0{\cdot}02$ A. Space group $P2_1$, $n = 2$. The axial ratios calculated from these dimensions are $a : b : c = 1{\cdot}435 : 1 : 1{\cdot}758$, in good agreement with those given above. On the strength of the *X*-ray determination, the optics and the conventions previously employed in the description of sterol crystals one would, however, prefer to assign a different β angle with consequent change in the cell dimensions to $a = 10{\cdot}69$, $b = 7{\cdot}45$, $c = 10{\cdot}84$ A., $\beta = 105° 24'$.

For the molecular weight determination the crystal density was measured by flotation in aqueous solutions of sodium chloride and of zinc sulphate, a centrifuge being used to hasten equilibrium. The value found was $1{\cdot}045 \pm 0{\cdot}003$ (somewhat higher than that of 1·01 given by Plzak and Rosicky). From this density and the above unit cell dimensions, and on the assumption of the presence of only the two molecules in the cell required by the symmetry, the molecular weight of fichtelite is calculated as 264 ± 4, in good agreement with the theoretical value, 262, required by the formula $C_{19}H_{34}$. This formula also agrees well (as does $C_{18}H_{32}$) with the molecular refractivity previously calculated by Neuhaus (*Ber.*, 1934, **67**, 1627) from the crystal refractive indices.

At this stage it is not possible to derive much more information from the preliminary *X*-ray examination in support of formula (II) for fichtelite. From the optic orientation and the general intensities of the *X*-ray reflections one may deduce the presence of roughly lath-shaped molecules placed with their lengths nearly normal to (001), along γ, and thickness in (110), which gives a very strong *X*-ray reflection. The dimensions of such molecules agree roughly with those required by either formula (I) or (II). But their arrangement, added to the low crystal density, is perhaps additional evidence in favour of the presence of a tertiary methyl group.—DEPARTMENT OF MINERALOGY, OXFORD. [*Received, July 7th*, 1938.]

The Estimation of Isomeric Nitrobenzoic Acids. By B. FLÜRSCHEIM and E. L. HOLMES.

To estimate the isomerides in a mixture of nitrobenzoic acids, we (J., 1928, 448) reduced it with titanous chloride (Knecht and Hibbert, *Ber.*, 1907, **40**, 3819), then brominated the amino-acids so as completely to eliminate carboxyl in the *o*- and *p*-acids, separated alkali-insoluble tribromoaniline from alkali-soluble tribromo-*m*-aminobenzoic acid, and weighed these. This gave accurate results, whereas Francis and Hill's titrimetric estimation of the bromine consumed in partial bromination (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) did not.

Ingold and Smith (this vol., p. 908), employing, *not our method of separating and weighing* the bromo-compounds formed, but Francis and Hill's method of titrating the bromine consumed, and having obtained poor results in the absence of a stable end-point of titration, proceeded to conclude that "the Francis–Flürscheim method of estimating nitro-compounds has not yet been described in a form to give results of high accuracy." Neither this conclusion, nor the description of our method as the "Francis–Flürscheim" method, can be accepted. Indeed it would be impossible to combine a titration of consumed bromine with our procedure (whereby all three isomerides take up three atoms of bromine) for the purpose for which our method was worked out, *viz.*, to determine the percentages of *m*- and of $(o + p)$-isomerides.—[*Received, July 12th*, 1938.]

The Stability of the Formic Acid Dimer. By E. A. MOELWYN-HUGHES.

THE following calculations have been made to see how far the stability of one of the best-known intermolecular complexes can be understood in terms of elementary electrostatic considerations. In the formic acid dimer, the separation ($r_{O, O}$) between the two oxygen atoms which form the hydrogen bond (Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419) is known to lie within the limits 2·55 and 2·85 A. (Brockway and Taylor, *Ann. Reports*, 1937, **34**, 213). Denoting the C=O bond of one molecule by A and the O—H bond of the second molecule by B, and accepting the usual values for the bond lengths (l_A = 1·16; l_B = 0·96 A.), dipole moments (μ_A = 2·5; μ_B = 1·6D.), and O=C—OH valency angle (125° 16′), we can show that, polarisation effects being neglected, the distance (r_{AB}) of the lines joining the centres of the attracting dipoles, and the angles (θ_A and θ_B) which they make with it, have the following values :

$r_{O,O}$ (A.)	2·85	2·55
r_{AB} (A.)	2·68$_7$	2·39$_3$
θ_A	51° 35′	50° 12′
θ_B	11° 3′	12° 26′
U (cals./mole)	− 4310	−6570

The last row gives the contribution of the dipole–dipole interaction to the energy of formation of the single bond, calculated as follows :

$$U = -\,2N_0\mu_A\mu_B \cos\theta_A \cos\theta_B/r^3(1 - l^2/r^2)$$

The results are sufficiently near to the experimental value of ΔH, which is — 7060 cals./bond (Coolidge, *J. Amer. Chem. Soc.*, 1928, **50**, 2166), to show the relevance of electrostatic effects (Moelwyn-Hughes and Sherman, J., 1936, 101).—[*Received, May* 31*st*, 1938.]

Interaction between Anthracene and Succinic Anhydride. By ERNST BERGMANN and (MISS) A. WEIZMANN.

COOK and ROBINSON recently reported the synthesis of 1′-methyl-1 : 2-benzanthracene, starting with anthracene and succinic anhydride (this vol., p. 505). We had performed the same synthesis up to the intermediate 1′-keto-1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthracene (which we obtained by means of phosphoric oxide instead of anhydrous stannic chloride), but, as the above condensation and reduction of the keto-acid formed had been described before by Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4355),* we did not publish our results, which are in excellent agreement with the data given by Fieser and Peters and by Cook and Robinson.

A few additional observations may be of interest. For recrystallisation of β-2-anthroylpropionic acid, we used butyl acetate. The *ethyl* ester of the acid had m. p. 138—140° after recrystallisation from benzene–light petroleum (Found : C, 78·1; H, 5·8. $C_{20}H_{18}O_3$ requires C, 78·4; H, 5·9%).

When the butyl acetate mother-liquor was evaporated nearly to dryness, and the residue extracted with boiling light petroleum (b. p. 80—100°), a part dissolved and was obtained, on cooling, as yellowish prisms, which had m. p. 125° after recrystallisation from alcohol and were, according to analysis, the isomeric β-1-*anthroylpropionic acid* (Found : C, 77·9; H, 5·0. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). Simultaneous substitution in both the 1- and the 2-position of anthracene has been observed in the analogous synthesis of acylanthracenes (I.G. Farbenindustrie A.G., *Chem. Zentr.*, 1928, I, 2209; 1930, I, 2630; compare Waldmann and Marmorstein, *Ber.*, 1937, **70**, 106).

The orientation of the β-2-anthroylpropionic acid was proved by its synthesis from 2-*bromoacetylanthracene* and ethyl sodiomalonate. 2-Acetylanthracene (1·5 g.) was suspended in anhydrous ether (60 c.c.), and bromine (0·5 c.c.; excess) added at 0°; reaction occurred at once. After 5 minutes, unchanged material (0·65 g.) was removed; from the filtrate, after some minutes, a greenish precipitate separated, which was collected and recrystallised several times from ethyl acetate, forming yellow needles, m. p. 155° (Found : C, 63·7; H, 3·6. $C_{16}H_{11}OBr$ requires C, 64·0; H, 3·7%). This substance was condensed with ethyl sodio-

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* Note by J. W. Cook.—In reporting our synthesis of 1′-methyl-1 : 2-benzanthracene Mrs. Robinson and I omitted to mention the prior work of Fieser and Peters on the preparation of β-2-anthroylpropionic acid and γ-2-anthrylbutyric acid. We regret this oversight and are glad to take this opportunity kindly afforded by Dr. Bergmann to acknowledge the priority of Fieser and Peters.

malonate (prepared from sodium and ethyl malonate in dry toluene), and the product hydrolysed by means of methyl-alcoholic potassium hydroxide. The small amount of acid thus obtained was shown by the method of mixed m. p. to be identical with the product (m. p. 222°) obtained from anthracene and succinic anhydride.

When a larger excess of bromine (1 c.c. instead of 0·5 c.c.) was used, a *tribromo*-compound (presumably 9 : 10-dibromo-2-bromoacetyl-9 : 10-dihydroanthracene) was obtained, which crystallised from benzene in yellow needles, m. p. 162° (Found : C, 42·1; H, 2·1. $C_{16}H_{11}OBr_3$ requires C, 41·9; H, 2·4%). Both bromination reactions gave poor yields.

Experiments to synthesise 2-halogenoacetylanthracenes directly have so far failed, anthracene and chloroacetyl chloride giving *x* : *y*-bischloroacetylanthracene. Chloroacetyl chloride (50 g.) was added gradually to a well-stirred mixture of anthracene (35·6 g.), tetrachloroethane (200 c.c.), and aluminium chloride (75 g.) at 0°. The mass was kept at room temperature for 12 hours and decomposed with ice and concentrated hydrochloric acid : a *bischloroacetylanthracene* (2 g.) separated spontaneously; after recrystallisation from ethyl malonate and toluene it formed prisms, m. p. 205° (Found : C, 65·6; H, 3·5. $C_{18}H_{12}O_2Cl_2$ requires C, 65·3; H, 3·6%). From the tetrachloroethane layer, nothing definite could be isolated.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, May 21st*, 1938.]
