TABLE II

POWDER PATTERN OF THE "CRYSTALLINE" TYPE BORON

B on W filament		B on Mo filament		Calculated	Miller's index
$\sin^2\theta$	I_{est}	$\sin^2\theta$	I_{est}	$\sin^2\theta$	
0.0190	2	0.0188	2	..	
0217	2	0218	1	0.220	
233	8	232	8	230	111
260	8	257	7	260	002
280	10	280	8	285	201
301	3	310	2	315	102
442	7	440	5	455	211
482	2	483	2	480	202
508	3	506	1	495	300
585	3	585	1	585	003
715	6	715	6	715	310
800	3	805	2	805	203
880	9	876	9	880	400
972	2	?		975	213
0.1040	8	0.1020	10	0.1040	132, 004
1110	3	1110	3	1110	231
1200	2	1205	2	1205	104
1310	4	1310	1	1305	130, 232
1416	3	?		1415	142
1444	7	1450	4	1440	501
1600	4	1600	2	1625	005
1910	6	1910	5	1920	404
1985	2	1995	4	1980	600
2150	2	?		2125	250, 243
2330	2	2300	1	2340	135, 006
2490	5	2480	5	2505	116, 405
2580	5	2610	3	2580	244
2800	3	2800	3	2780	145
2900	6	2900	5	2900	442
3130	4	3120	3	3110	335
3250	5	3260	6	3225	443

TABLE III

POWDER PATTERN OF THE "AMORPHOUS" (SCHUCHARD) BORON

$\sin^2\theta$	I_{est}
0.0279	4
.0340	10
422	4
500	1
575	6
715	2
945	2
0.1170	3
1460	2
2420	1
2860	2
3130	1

pieces of steel were continuously circulated on the surface by means of an outer magnetic field. This method enabled us to carry out experiments with extremely small quantities of liquid boron tribromide. Constant stream of boron tribromide vapor was secured by the sole control of liquid boron tribromide temperature. Electrodes were made of Pt, and Mo and W filaments of different thicknesses were used alternatively. Deposits which formed a dense cylindrical layer around the W or Mo core were obtained. In no case could the deposit be stripped from the filament by simple means.

On both W and Mo two virtually different deposits resulted depending on the temperature of the filament during the process. At lower temperatures, 1000–1300° "graphitic," grayish, virtually amorphous deposits were obtained, while around 1500–1600° dark gray crystalline surfaces resulted. Single crystal growth was observed in a few cases, but the specimens were too small, 0.2–0.3 mm., for further investigations. (Apparently the reduction of boron tribromide with hydrogen is more favorable for the growth of single crystals.) The diameter of boron coated Mo and W filaments after thirty to sixty minutes of decomposition varied between 400–500 μ, while the core diameter was 50–100 μ. We were not able to check the purity of our samples thoroughly, however there is good reason to believe that the purity of our samples was not inferior to those of other investigators. Specific density measurements averaged 2.33 (possible error ±0.02). Electrical conductivity and general chemical behavior were qualitatively investigated. Our findings substantially agree with the data of Laubengayer, *et al.*

2. X-Ray Powder Diffraction Pattern.—All boron collected on the W and Mo filaments was investigated in a 5-cm. radius cylindrical camera with Cu Kα-ray. We found it unnecessary to eliminate the W or Mo filaments since X-ray patterns of W and Mo could easily be singled out. As mentioned previously, we obtained two types of deposits on both Mo and W. These gave different X-ray patterns; however, the same type of deposit on the two filament materials gave identical ones, so that there was no disturbing effect due to any alloy formation between boron and the filament material.

The reflections of the "graphitic" type of boron coating could be indexed using a tetragonal elementary cell (a = 8.57 Å., c = 8.13 Å., 78 atoms/cell (Table I).

The "crystalline" deposit gave a pattern which suggested a hexagonal cell (a = 11.98 Å., c = 9.54 A., 180 atoms/cell) (Table II).

X-Ray patterns were taken from the "amorphous" boron which was used for the preparation of boron tribromide (supplied by the Schuchard Ltd., Germany); 12 line pairs were observed (Table III).

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Interpretation of the Parachor

BY M. S. TELANG

Sugden's parachor P is based on Macleod's empirical equation[1]

$$\gamma = C(D - d)^4 \tag{1}$$

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(1) D. B. Macleod, *Trans. Faraday Soc.*, **19**, 38 (1923).

where γ is the surface tension, D and d are the orthobaric densities of the liquid and vapor, respectively, and C is a constant, different for each liquid. Fowler[2] has partially succeeded in its derivation in the neighborhood of the critical temperature. Ferguson and Kennedy[3] give a variant of (1) as

$$\gamma = C(D - d)^p \qquad (2)$$

where $p \approx 4$. Taking out logarithms of (2),

$$\log \gamma = \log C + p \log (D - d) \qquad (3)$$

The plot of log γ *vs.* log $(D-d)$ is linear with p as the slope and log C as the intercept on the log γ-axis. From (1), Sugden[4] obtains

$$M/(D - d) \times \gamma^{1/4} = MC^{1/4} = P \qquad (4)$$

where M is the molecular weight, considering it to be a comparative molecular volume at equal internal pressures; *i. e.*, P reduces to $M/(D-d)$ when $\gamma = 1$. In practice, γ approaches unity in the vicinity of the critical temperature, where d becomes appreciable, giving $M/(D-d) \gg M/D = V$; *e. g.*, $\gamma \approx 1$ for benzene at 270° ($t_{\text{crit.}} = 288.5°$). At this temperature, $M/(D-d) = 211.0$ and $M/D = 156.5$, indicating that to call P as a molecular volume is untenable. Ferguson[5] objects to its being called a volume from its dimensional analysis. While we can understand the molecular volume being additive, it is difficult to attribute constitutive properties to it. Reverting to (3), since log C = log γ when log $(D - d) = 0$, C is the surface energy when $D - d = 1$. This should be the normal interpretation applying the principles of analytical geometry. Since P is based on C with a fractional exponent $^1/_4$, it is difficult to give its full rational significance. The additive-constitutive nature of energy is not difficult to follow since we have the parallel cases of molecular heat employing Kopp's rule[6] and of the lattice energy in crystals.

Kopp's law of the additivity of molecular volumes, the fore-runner of Sugden's parachor, can be shown to be, in reality, a law of the additivity of energy. The molecular volume can be written as[7]

$$V = (2N/(3)^{3/4}) \times (\Delta\epsilon_s)^{3/2}/(\gamma)^{3/2} \qquad (5)$$

where $\Delta\epsilon_s$ is the surface energy per molecule and N is the Avogadro number. It has been observed that for many liquids, $\gamma \approx 21$ dynes/cm. at the boiling points, at which Kopp compared his molecular volumes. So, (5) reduces to

$$V \approx \text{constant} \times (\Delta\epsilon_s)^{3/2} \qquad (6)$$

where the constant is $2N/(3^{3/4} \times 21^{3/2})$. Thus, in reality, Kopp compared surface energies and not molecular volumes, contrary to the general belief. Obviously, the limitations of this law are due to γ being not the same for all liquids at their boiling points. The view that surface energies are additive and constitutive is supported by the additivity of molar surface energies at the absolute zero given by Ferguson and Kennedy.[3] It is to be noted here also that γ for many liquids does not differ very appreciably from the mean value of 68 dynes/cm. at the absolute zero.[8]

We may tentatively derive an approximate form of Macleod's equation under certain limited conditions. With a uniform and close packing of molecules in liquids, the number of contacts with the closest neighbors for a molecule in the surface and for one in the liquid phase are 9 and 12, respectively. The number of molecules per sq. cm. in the surface is $2/(r^2\sqrt{3})$, r being the average distance between the centers of the closest neighbors. So, the free energy involved in the formation of one sq. cm. of surface will be

$$\gamma = (2/(\gamma^2\sqrt{3})) \times \left(\frac{12 - 9}{2} \times U\right) \qquad (7)$$

where $-U$ is the potential energy of interaction for a pair of molecules at the distance, r.[9] The potential energy of a pair of molecules may be expressed as

$$U = -Ar^{-m} + Br^{-n} \qquad (8)$$

where the first term on the right-hand side represents the attractive energy and the second the repulsive energy for various intermolecular separations. When molecules are very closely packed so as to force them almost into mutual contact, a condition which may exist at very low temperatures or in a highly compressed state, r becomes relatively smaller, and repulsion becomes predominant. Under such circumstances, we may reasonably reduce (8) to the approximate form

$$U \approx Br^{-n} \qquad (9)$$

neglecting the term due to attraction. Incorporation of (9) in (7) gives

$$\gamma \approx \sqrt{3}B/(r)^{n+2} \qquad (10)$$

Substituting for r[7]

$$\gamma \approx \sqrt{3}B(N/\sqrt{2}M)^{(n+2)/3}D^{(n+2)/3} \qquad (11)$$

Putting $\sqrt{3}B(N/\sqrt{2}M)^{(n+2)/3} \approx C$, we have

$$\gamma \approx CD^{(n+2)/3} \qquad (12)$$

Neglecting d at low temperatures and taking $n = 10$ on the average, $(n + 2)/3 = p = 4$ is the index of Macleod's equation. Thus

$$C^{1/4} \approx (\sqrt{3}B)^{1/4}/(\sqrt{2}) \times N/M \qquad (13)$$

Hence, P is given by

$$MC^{1/4} \approx (\sqrt{3}B)^{1/4}/(\sqrt{2}) \times N \qquad (14)$$

---

(2) R. H. Fowler, *Proc. Roy. Soc.* (*London*), **A159**, 229 (1937).

(3) A. Ferguson and S. J. Kennedy, *Trans. Faraday Soc.*, **32**, 1474 (1936).

(4) S. Sugden, "The Parachor and Valency," London, Routledge, 1930, p. 30.

(5) A. Ferguson, *Nature*, **125**, 597 (1930).

(6) S. Glasstone, "Text-book of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 415.

(7) M. S. Telang, *J. Chem. Phys.*, **17**, in press (1949).

(8) S. Sugden, *J. Chem. Soc.*, 1784 (1927); M. S. Telang, *Curr. Sci.*, **12**, 19 (1943).

(9) J. W. Belton and M. G. Evans, *Trans. Faraday Soc.*, **41**, 1 (1945); E. A. Guggenheim, *ibid.*, **41**, 150 (1945); R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939, p. 422.

Multiplication of (13) by M giving the right-hand side of (14) retains only one parameter B for comparing various substances in the form of P. Although B is a proportionality constant, it possesses the dimensions of energy and not of volume. The term B can be expected to be constitutive since it depends upon the atomic and molecular configurations.

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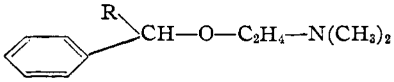
Basically Substituted Pyrimidine and Imidazoline Derivatives as Histamine Antagonists

BY CHARLES H. TILFORD, M. G. VAN CAMPEN, JR., AND ROBERT S. SHELTON

A recent report[1] from this Laboratory showed the effectiveness of 2-[α-(2-dimethylaminoethoxy)-α-methylbenzyl]-pyridine (I) as an antihistaminic agent. The dimethylaminoethyl ethers of α-phenyl-4-methyl-6-methoxy-2-pyrimidinemethanol and α-phenyl-2-imidazolinemethanol have now been prepared and when tested *in vitro* were about 0.0025 as active as I.



R	Free base B. p. °C.	Free base B. p. Mm.	Free base Yield, %	Hydrochloride Formula	Hydrochloride M. p., °C. (cor.)	Hydrochloride % Halogen[a] (ionizable) Calcd.	Hydrochloride % Halogen[a] (ionizable) Obs.	Hydrochloride Activity,[b] γ/ml.
4-Methyl-6-methoxy-2-pyrimidyl	135–140	0.2	30	$C_{17}H_{23}O_2N_3 \cdot HCl$	149–151	10.49	10.40	20
				$C_{17}H_{23}O_2N_3 \cdot 2HCl$	176–178	18.95	18.90	20
2-Imidazolinyl	155–160	0.08	63	$C_{14}H_{21}ON_3 \cdot 2HCl$	246–247	22.14	22.0	20

[a] Determined by titration with silver nitrate using dichlorofluorescein indicator. [b] Minimal concentration of test compound necessary to antagonize 0.1 γ/ml. of histamine diphosphate on isolated guinea pig intestine.

Experimental

α-Phenyl-4-methyl-6-methoxy-2-pyrimidinemethanol.—To a stirred solution of 50 g. (0.23 mole) of α-phenyl-4-methyl-6-hydroxy-2-pyrimidinemethanol[2] in 300 ml. of 4% sodium hydroxide was added 34 g. (0.28 mole) of dimethyl sulfate over a period of thirty minutes at 50–60°. The reaction mixture was then stirred and heated on the steam-bath at 90–95° for two hours, made alkaline with 60 ml. of 10% sodium hydroxide, and extracted with 250 ml. of toluene. From the aqueous layer, 15 g. of unchanged starting pyrimidinemethanol was obtained by acidifying with glacial acetic acid and collecting the precipitate at the filter. The toluene extract was treated with a slight excess of alcoholic hydrochloric acid, cooled to −20°, and filtered. The yield of crude product melting at 153–156° (dec.) was 27 g. (63% based on unrecovered original pyrimidinemethanol). A sample was recrystallized from a butanone–ethanol mixture to give white crystals melting at 172–175° (dec.).

Anal. Calcd. for $C_{13}H_{14}O_2N_2 \cdot HCl$: Cl, 13.3. Found: Cl, 13.3.

α-Phenyl-2-imidazolinemethanol.—The procedure of Brockmuhl and Knoll[3] was followed using 71 g. (0.33 mole) of ethyl mandelimidate hydrochloride[4] and 20 g. (0.33 mole) of anhydrous ethylenediamine. The yield of crude base melting at 182–186° was 51 g. (88%). A sample was recrystallized from a butanone–ethanol mixture giving white crystals melting at 184–186°. The white crystalline hydrochloride was prepared and melted at 224–226°.

Anal. Calcd. for $C_{10}H_{12}ON_2 \cdot HCl$: Cl, 16.68. Found: Cl, 16.60

Aminoethers.—The general method of preparation is given in reference 1.

DEPARTMENT OF ORGANIC CHEMISTRY
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RECEIVED NOVEMBER 5, 1948

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[1] Tilford, Shelton and Van Campen, THIS JOURNAL, **70**, 4001 (1948).

[2] Pinner, *Ber.*, **23**, 2948 (1890).

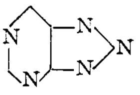
[3] Brockmuhl and Knoll, U. S. 1,999,989 (1931).

[4] Mackenzie, *J. Chem. Soc.*, **113**, 2 (1918).

Triazolo and Imidiazopyridines

BY J. R. VAUGHAN, JR., J. KRAPCHO[1] AND J. P. ENGLISH

The preparation and antibacterial properties of 1-*v*-triazolo[d]pyrimidines (I) substituted analogously to the naturally-occurring purines (II) have been reported.[2] Since the *in vivo* activities of those compounds were not very striking, attention was turned to two other nuclei, both isoelectronic with the purine nucleus as is 1-*v*-triazolo[d]-pyrimidine. This involved substituting a pyridine ring for the pyrimidine ring of the purines and the triazolo[d]pyrimidines, giving imidazo-[b]pyridines (III) and pyrido[2,3-d]*v*-triazoles (IV), respectively.



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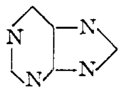

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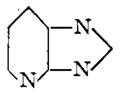
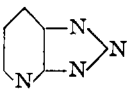


III



IV

None of the compounds prepared (see Table I) showed antibacterial activity against strains of *Mycobacterium*, *Erssipelothrix*, pneumococcus streptococcus and *Pasteurela multocida*.[3]

The common starting material for these compounds is 2,3-diaminopyridine or some substituent thereof. The use of 5-chloro-2,3-diaminopyridine was much more satisfactory for a number of reasons. The development of an improved procedure for the preparation of 2-amino-5-chloro-

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[2] Roblin, Lampen, English, Cole and Vaughan, THIS JOURNAL, **67**, 290 (1945).

[3] Tested under the direction of Dr. Harold J. White of these laboratories.