

TABLE I
THE EMISSION OF POSITRONS AND ELECTRONS

	$\Delta M_{\text{Exptl.}}^a$	ΔM_F	Bond
${}^1\text{H} = n^1 + e^+$	0.0021	-0.0002	0.0023
${}^3\text{He} = \text{H}^3 + e^+$.0011	-.0011	.0022
${}^9\text{Be} = \text{Be}^9 + e^+$	-.0003	-.0027	.0024
${}^{11}\text{C} = \text{B}^{11} + e^+$	-.0013	-.0033	.0020
${}^{13}\text{N} = \text{C}^{13} + e^+$	-.0015	-.0037	.0022
${}^{15}\text{O} = \text{N}^{15} + e^+$	-.0021	-.0043	.0022
${}^{17}\text{F} = \text{O}^{17} + e^+$	-.0025	-.0047	.0022
$\text{Li}^8 = {}^7\text{Be}^8 + e^-$	-.0112	.0031	-.0143
$\text{B}^{12} = {}^{12}\text{C}^{12} + e^-$	-.0117	.0043	-.0160
$\text{N}^{16} = {}^{16}\text{O}^{16} + e^-$	-.0070	.0052	-.0122
$\text{F}^{20} = {}^{20}\text{Ne}^{20} + e^-$	-.0064	.0059	-.0123
$n^1 = {}^1\text{H}^1 + e^-$	-.0010	.0012	-.0022

^a Fowler, Delsasso and Lauritsen, *Phys. Rev.*, **49**, 561 (1936). The ΔM for the non-radioactive reactions are from Ref. 1. The masses of e^+ and e^- have been included in ΔM_F .

TABLE II
THREE TYPES OF NUCLEAR REACTIONS

	$\Delta M_{\text{Exptl.}}$	ΔM_F	Bond
$\text{H}^3 + \text{H}^1 = \text{He}^4$	-0.0213	0.0006	0.0219
$\text{Li}^7 + \text{H}^1 = \text{Be}^8$	-.0183	.0016	.0199
$\text{B}^{11} + \text{H}^1 = \text{C}^{12}$	-.0173	.0025	.0198
$\text{N}^{15} + \text{H}^1 = \text{O}^{16}$	-.0129	.0036	.0165
$\text{F}^{19} + \text{H}^1 = \text{Ne}^{20}$	-.0140	.0043	.0183
$\text{He}^3 + n^1 = \text{He}^4$	-.0223	-.0002	.0221
$\text{C}^{11} + n^1 = \text{C}^{12}$	-.0198	-.0004	.0194
$\text{C}^{13} + \text{H}^1 = \text{N}^{13}$	-.0021	.0031	.0052
$\text{O}^{16} + \text{H}^1 = \text{F}^{17}$	-.0008	.0040	.0048
$\text{C}^{12} + n^1 = \text{C}^{13}$	-.0054	-.0003	.0051
$\text{O}^{16} + n^1 = \text{O}^{17}$	-.0045	-.0004	.0041
$\text{H}^2 + \text{H}^2 = \text{He}^4$	-.0255	.0007	.0262
$\text{Li}^6 + \text{H}^2 = \text{Be}^8$	-.0236	.0015	.0251
$\text{B}^{10} + \text{H}^2 = \text{C}^{12}$	-.0275	.0026	.0301
$\text{N}^{14} + \text{H}^2 = \text{O}^{16}$	-.0220	.0034	.0254

TABLE III
THE FORMATION OF $4n$ NUCLEI FROM He^4

	$\Delta M_{\text{Exptl.}}$	ΔM_F	Bond	
			Calcd.	Model
$2\text{He}^4 = \text{Be}^8$	-0.000	+0.0024	0.0024	0.005
$3\text{He}^4 = \text{C}^{12}$	-.081	.0065	.0146	.015
$4\text{He}^4 = \text{O}^{16}$	-.156	.0121	.0277	.030
$5\text{He}^4 = \text{Ne}^{20}$	-.021	.0191	.0402	.042
$7\text{He}^4 = \text{Si}^{28}$	-.041	.037	.078	.083

Three types of reactions are given in Table II: (1) the addition of a mass particle, proton or neutron, to a $4n + 3$ nucleus, (2) the addition of a mass particle to a $4n$ nucleus and (3) the addition of H^2 to a $4n + 2$ nucleus. With few exceptions the bond energies for each group are constant within the experimental error. Many other examples may be given showing the same general constancy.

Latimer and Libby (Ref. 1) calculated the mass

defect for a number of the heavier nuclei using Latimer's nuclear model, but the present accepted mass of He^4 necessitates a revision of those calculations and, in fact, requires the use of the experimental values of the radii instead of the somewhat smaller values which they used. A summary of the calculated bond energies and the comparison with the values predicted by the model for the lighter elements is given in Table III. The bond energies used are 0.005 for the bond between two mass particles and 0.017 between three particles. It should be emphasized that these values in terms of the model are not entirely arbitrary, the first is taken as $1/6$ of the total experimental bond energy of He^4 , 0.031 M units, since in a tetrahedron there are six pairs of interactions, and the second is approximately $1/2$ the He^4 value.

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TRANS- AND CIS-AS-OCTAHYDROPHENANTHRENE Sir:

The hydrocarbon skeleton of morphine (or more correctly that of dihydromorphine) consists principally of a 1,2,3,4,9,10,11,12-octahydrophenanthrene (*as*-octahydrophenanthrene) nucleus, and therefore the preparation of derivatives of this hydrocarbon carrying functional groups of the morphine molecule has been undertaken. Amino alcohols derived from symmetric octahydrophenanthrene were described in a recent communication [van de Kamp and Mosettig, *THIS JOURNAL*, **57**, 1107 (1935)].

In the preparation of *as*-octahydrophenanthrene according to the synthetic methods known so far, either the *cis*- or the *trans*-form, or more likely a mixture of the two, can be expected. As far as we know no statements concerning the configuration of this hydrocarbon have been made previously. We prepared the *as*-octahydrophenanthrene by effecting the dehydration and the isomerization of 1- β -phenylethylcyclohexanol [prepared according to Cook and Hewett (*J. Chem. Soc.* 1098 (1933))] with phosphorus pentoxide in one step. The yield in this last step calculated on the carbinol, was 90%. Phosphorus pentoxide has already been employed by Bardhan and Sengupta [*J. Chem. Soc.*, 2520 (1932)] in the ring closure of 2- β -phenylethylcyclohexanol.

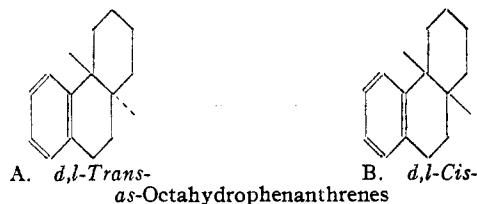
The product thus obtained, after refluxing with sodium and distilling off, was fractionated, using a Widmer fractionating column.

By repeated fractionation (until constancy of physical data was reached) the *as*-octahydrophenanthrene was separated into two main fractions, A and B, and a relatively small mixed fraction.

TABLE I

Fraction	A (20%)	B (70%)
B. p., { °C.	135.5-135.7	142.6-142.8
{ Mm.	10.5-10.8	9.2
Refr. index	n_D^{15} 1.5460	n_D^{10} 1.5592
d_4^{25}	0.9828	1.0053

From a comparison of the above data with those of *trans*- and *cis*-decahydronaphthalene [Hückel, *Ann.*, **441**, 42 (1925)], we assign by analogy to the hydrocarbon A the *trans*-configuration and to the hydrocarbon B the *cis*-configuration.



It is possible that on repeating this separation on a larger scale, we will obtain slightly different and better physical data on the isomeric *as*-octahydrophenanthrenes. Furthermore, the possibility that one of the fractions may be a constant boiling mixture, still remains. We have prepared from each of the isomers a methyl ketone, its semicarbazone, and the carboxylic acid by oxidation of the methyl ketone.

TABLE II
DERIVATIVES OF*trans*- AND *cis*-*as*-OCTAHYDROPHENANTHRENE

	<i>Trans</i> -. m. p., °C.	<i>Cis</i> -. m. p., °C.
—COCH ₃	94-94.5	Oily
—semicarbazone	230-231.5	211-213
mixed m. p.	192-203	
—COOH	226-228	230-232
mixed m. p.	180-190	

We wish to mention the remote possibility that the acetyl group and consequently the carboxyl group are attached in different positions in the two hydrocarbons. Furthermore, it has to be taken into account that, in the Friedel-Crafts reaction, partial isomerization may have taken place through the action of the aluminum chloride [*cf.*

Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1299 (1932)].

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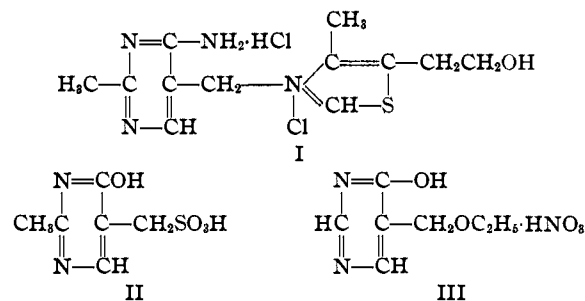
JACOB VAN DE KAMP
ERICH MOSETTIG

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STRUCTURE OF VITAMIN B₁

Sir:

Certain provisional features of the structure previously proposed [THIS JOURNAL, **57**, 229 (1935)] require revision. We now feel justified in proposing Structure I for the vitamin.



We obtained by liquid ammonia cleavage of the vitamin a free base, C₆H₁₀N₄, which gives a double banded absorption quite different from the single bands of 2,6, 4,6 or 5,6-diaminopyrimidines but closely akin to those of 5-alkyl 6-amino pyrimidines. (Alkyl groups in position 5 have a profound influence on absorption of 6-amino pyrimidines; alkyls in other positions have minor effects.) The ultraviolet absorption of an extended series of pyrimidines provided convincing evidence that the second amino group of the base, C₆H₁₀N₄, is in a side chain. This base forms a dipicrate, m. p. 225°, presumably identical with the picrate of Windaus [*Z. physiol. Chem.*, **237**, 100 (1935)].

My associate, Dr. J. K. Cline, was also able to obtain from the amino sulfonic acid [THIS JOURNAL, **57**, 1093 (1935)] by the action of sodium in liquid ammonia a small yield of a base, C₆H₉N₃, which was identified by mixed melting points of the picrates, 221°, as 2,5-dimethyl-6-aminopyrimidine which was synthesized for absorption studies. This is the first identified pyrimidine to be obtained from the vitamin. Its significance was greatly enhanced by subsequent synthesis of II which is undistinguishable by any known means from the oxy sulfonic acid of natural origin [Ref. 3].

We have synthesized five new ethoxy derivatives of 6-oxypyrimidine; others are described