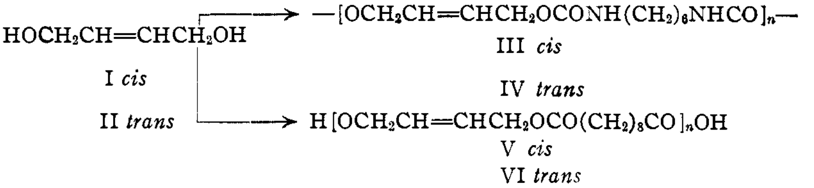
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Effect of *cis* and *trans* Olefinic Groups on the Properties of Polyurethans and Polyesters[1]

BY C. S. MARVEL AND CHARLES H. YOUNG[2]

In a previous paper[3] the effect of replacing a regularly recurring $-CH_2CH_2-$ unit in a polymer by a $—C{\equiv}C—$ unit has been reported. As a continuation of this research the *cis* and *trans* isomers of 2-butene-1,4-diol have been prepared and converted to polyurethans by reaction with hexamethylene diisocyanate, and to polyesters by reaction with sebacic acid.



$HOCH_2CH{=}CHCH_2OH$ I *cis*, II *trans*

$\rightarrow -[OCH_2CH{=}CHCH_2OCONH(CH_2)_6NHCO]_n-$ III *cis*, IV *trans*

$\rightarrow H[OCH_2CH{=}CHCH_2OCO(CH_2)_8CO]_nOH$ V *cis*, VI *trans*

The *cis*-2-butene-1,4-diol (I) was prepared in 80% yield by the low-pressure, Raney nickel-catalyzed hydrogenation of 2-butyne-1,4-diol. Although the reaction was interrupted after the addition of one mole of hydrogen, careful fractionation was required to obtain the product free from 1,4-butanediol. The synthesis of the *trans*-2-butene-1,4-diol (II) was accomplished in 66% over-all yield from butadiene. The *trans*-1,4-dibromo-2-butene was prepared and converted to *trans*-1,4-diacetoxy-2-butene, which in turn was converted to the *trans*-glycol by alcoholysis with ethanol and sodium ethoxide.

The polyurethans (III, IV) were prepared according to the procedure previously described[4] for the polymer from 1,4-butanediol. Copolymers of hexamethylene diisocyanate and mixtures of 1,4-butanediol and *cis*- and *trans*-2-butene-1,4-diol in the ratio of 80:20 and 20:80 were also prepared in order that Flory's[5] method of determining the heat and entropy of fusion by measuring melting point depressions could be applied to these polymers. The polymers containing high percentages of the *cis* glycol were purified by recrystallization from 90–10 methanol–dimethylformamide solution because of their considerably greater solubility in the usual 50–50 mixture. For comparative purposes polymers of similar viscosity (0.1 to 0.2) were used.

The *cis* and *trans* polyesters (V, VI) were prepared by direct esterification of the glycols (I, II) with sebacic acid. Although polymers of like viscosity were not obtained, the values were of the same order of magnitude (0.56 and 0.30, respectively).

The polymers were characterized by determining their infrared absorption curves[6] and X-ray diffraction patterns.[7]

The infrared spectra of the *trans*-, *cis*- and mixed *cis*-polyurethans as finely ground suspensions in Nujol are recorded in Fig. 1. In Fig. 2 are recorded the spectra of the polyesters, which were obtained on a melt of the polymer. The absorption bands at 1380, 1460 and 2900 cm.$^{-1}$ are due to the Nujol, while the absorption at 1700 cm.$^{-1}$ is the characteristic carbonyl band. The polyurethans also exhibit the amide absorption at 1530 and 3300 cm.$^{-1}$. In the *trans*-polyurethan (IV) the double absorption band at 970 and 987 cm.$^{-1}$ is thought to be due to the *trans* configuration around the double bond, while in the *cis* isomer (III) the double bond absorption appears as a broader band at 975–980 cm.$^{-1}$. This band decreases in intensity and finally disappears in polymers containing smaller percentages of the *cis* diol. Conversely, as the percentage of 1,4-butanediol increases the carbon–carbon single bond absorption at 995, 1064 and 1220 cm.$^{-1}$ becomes increasingly apparent. In the case of the polyesters, differences ascribable to *cis–trans* isomerism are less readily apparent. There is only a slight indication of the *trans* doublet at 970 and 987 cm.$^{-1}$, but the *cis* absorption at 975 cm.$^{-1}$ is well defined.

The X-ray powder diffraction patterns of the polymers were determined with a Norelco X-ray spectrometer using copper Kα radiation. The results are recorded in Table I and Figs. 3 and 4.

TABLE I

X-RAY DIFFRACTION ANALYSES

Peak angle[a] (degrees)	*d* Spacing (ångstroms)	Peak angle (degrees)	*d* Spacing (ångstroms)
cis-Polyurethan		*trans*-Polyurethan	
10.6	8.32	11.0	8.00
20.8	4.28	21.2	4.18
24.0	3.71	24.4	3.63
cis-Polysebacate		*trans*-Polysebacate	
9.6	9.16	9.6	9.16
21.0	4.23	20.4	4.35
24.4	3.63	21.8	4.08
		24.6	3.62

[a] The peak angle is 2 θ or two times the angle of diffraction.

Each of the measured peaks is an indication of a crystalline plane within the molecule. The data show that a fairly high degree of crystallinity is present in both the polyurethans and the polyesters, although slightly higher in the latter. Both *cis* and

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[2] Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, South Charleston, W. Va.

[3] C. S. Marvel and J. H. Johnson, THIS JOURNAL, **72**, 1674 (1950).

[4] Otto Baeyer, private communication, 1947; B.I.O.S. Final Reports 1947 and 1948; C.I.O.S. Final Report XXIX-12 (Appendix).

[5] P. J. Flory, *J. Chem. Phys.*, **15**, 684 (1947).

[6] We are indebted to Miss Elizabeth Petersen for the infrared absorption curves and their interpretation.

[7] We are indebted to Professor G. L. Clark and Mr. J. Fuchs for the X-ray patterns.

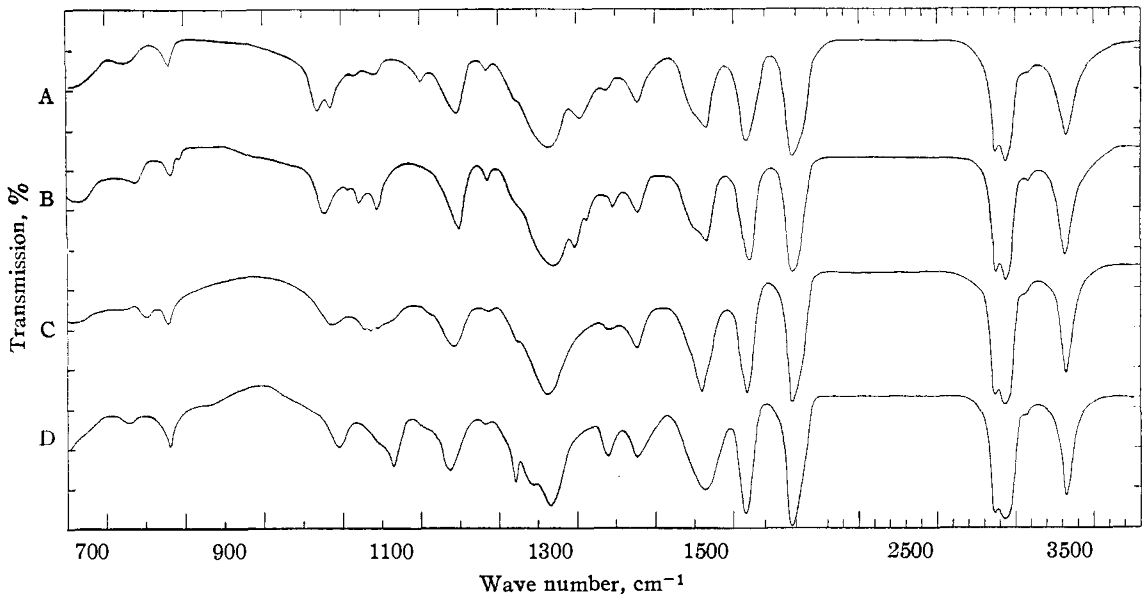

Fig. 1.—Infrared absorption curve of polyurethans: A, polyurethan 10 (all *trans*, 0-100T); B, polyurethan 11 (all *cis*, 0-100C); C, polyurethan 22 (mixed *cis*, 20-80C); D, polyurethan 24 (mixed *cis*, 80-20C).

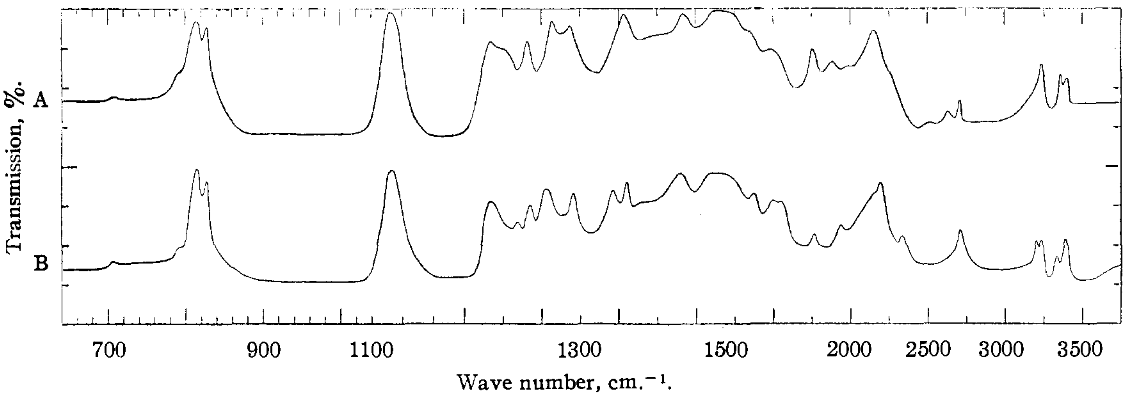

Fig. 2.—Infrared absorption curves of polyesters: A, polyester from *trans*-2-butene-1,4-diol; B, polyester from *cis*-2-butene-1,4-diol.

trans isomers give similar patterns. Comparison of these patterns with those of butanediol and butynediol polymers[3] indicates a good degree of similarity, although the earlier polyurethans are somewhat more amorphous.

In order to obtain information on the low tem-

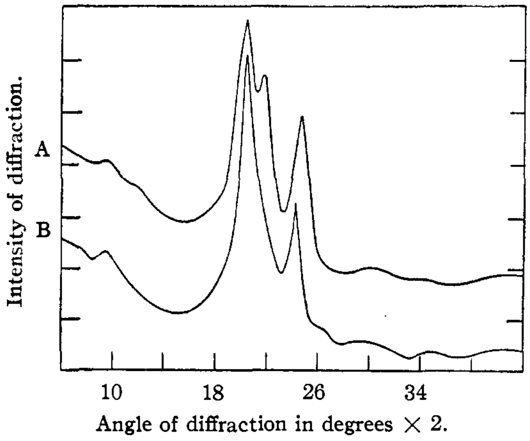

Fig. 3.—X-Ray diffraction patterns: A, polyhexamethylenediurethan from *cis*-2-butene-1,4-diol; B, polyhexamethylenediurethan from *trans*-2-butene-1,4-diol.

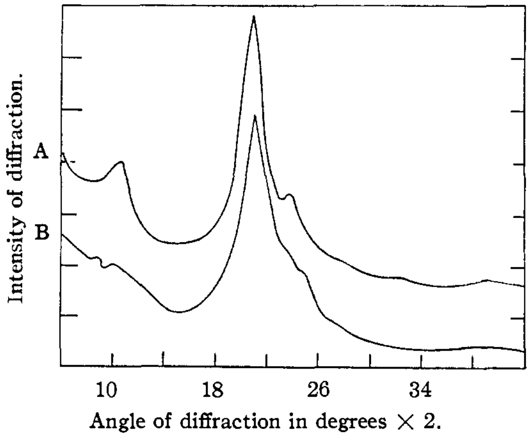

Fig. 4.—X-Ray diffraction patterns: A, polysebacate from *trans*-2-butene-1,4-diol; B, polysebacate from *cis*-2-butene-1,4-diol.

perature behavior of the polymers, second order transition temperature determinations were made according to the procedure of Bekkedahl.[8] These data are reported in Table II; the values for butanediol and butynediol polymers are included for comparison.[3]

Table II

Second Order Transition Temperatures

Polymer	Capillary m. p., °C.[9]	Transition temp., °C.
Polyurethan of:		
butane-1,4-diol	176–177	−58
trans-2-butene-1,4-diol	175–177	−44
cis-2-butene-1,4-diol	134–136	−39
2-butyne-1,4-diol	149–150	−45
Polyester of:		
butane-1,4-diol	64–64.5	−57
trans-2-butene-1,4-diol	68–69.5	−40
cis-2-butene-1,4-diol	58–59	−41
2-butyne-1,4-diol	51–53	−27

The second order transition temperature (sometimes considered as an internal melting point) is a measure of the temperature at which the amorphous areas assume dimensional stability and the polymer becomes stiff and rigid. Both *cis* and *trans* double bond structures impart a degree of rigidity not present in the saturated polymer, but, in the case of the polyesters, less than that of the triple bond.

The thermodynamic values for the polyurethans which were calculated from Flory's equation[5] are reported in Table III.

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Table III

Physical Constants and Thermodynamic Values for Polyurethans of Butene-1,4-diol, *cis* and *trans*-2-Butene-1,4-diol, and Mixtures

Polyurethan, satd.[n] unsatd., *cis*	Inherent viscosity	Value used for m. p., °C.	Calcd. heat of fusion, cal.	Calcd. entropy of fusion, cal./deg.
100–0	0.17	175	8350	18.6
90–10	.11	170		
20–80	.10	121		
0–100	.12	136	4750	11.6
trans				
100–0	.17	175	6600	14.8
80–20	.11	162		
20–80	.12	157		
0–100	.19	177	4250	9.5

The data in Table III must be regarded as approximate since the melting points of the copolymers are not too sharp. The fact that the apparent heats and entropies of fusion of the 100–0 polymer are not the same for the two calculations may be due to this cause or it may indicate that the copolymers do not behave as if they were ideal solutions. These data indicate that while the *cis* and *trans* olefinic polymers exhibit about the same degree of rigidity, they are stiffer than the corresponding saturated analog. This is in agreement with the findings of both second order transition temperature determinations and X-ray diffraction patterns, that there is little difference in physical properties of the polymers which may be attributed to *cis–trans* isomerism.

Experimental

***cis*-2-Butene-1,4-diol.**—A solution of 17.2 g. (0.2 mole) of 2-butyne-1,4-diol in 100 ml. of methanol was hydrogenated over Raney nickel in a calibrated apparatus at 25° and 3 atm. until 1.0 mole of hydrogen had been absorbed. After removal of the catalyst by filtration, the crude products from 4 runs were combined and fractionated through a Fenske column at a 20:1 reflux ratio to give 56.4 g. (80% yield) of *cis*-2-butene-1,4-diol, b.p. 100–102° (2.0 mm.); n^{20}D 1.4782.

The dibenzoate ester was obtained as a light brown solid, even after 4 recrystallizations from ethanol, m.p. 65–66° (reported, 69°[10]).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.00; H, 5.44. Found: C, 72.41; H, 5.49.

***trans*-2-Butene-1,4-diol.**—*trans*-1,4-Dibromo-2-butene was prepared from butadiene and converted to *trans*-1,4-diacetoxy-2-butene according to general procedures described in Hickinbottom.[11] The *trans*-glycol was obtained from the diester by alcoholysis. A mixture of 85 g. (0.495 mole) of the diacetate and 230 g. (4.95 moles) of absolute ethanol containing 4.0% of sodium ethoxide was refluxed overnight, after which the ethyl acetate and most of the ethanol were removed by distillation. Water was added and the distillation continued to a head temperature of 98° to ensure complete removal of the ethanol. The alkaline residue was then extracted continuously with ether for 48 hours. Evaporation of the ether and distillation of the residue gave 37 g. (85% yield) of *trans*-2-butene-1,4-diol, b.p. 102–104° (2.5 mm.); n^{20}D 1.4775.

The dibenzoate ester was obtained as a white solid after one recrystallization from ethanol, m.p. 99–100° (reported, 101°[12]).

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.00; H, 5.44. Found: C, 72.67; H, 5.58.

Polyurethans.—The polyurethans were synthesized according to the procedure of Marvel and Johnson.[3] In the purification of the products containing a high percentage of the *cis*-glycol by recrystallization from methanol–dimethylformamide solution, the solvent mixture was changed from 50–50 to 90–10 because of the high solubility of the polymer in the former solution. The inherent viscosity of the polymers was determined on a 0.4% solution in *m*-cresol at 25.5°.

Polyurethan from *cis*-2-Butene-1,4-diol and 1,6-Hexamethylene Diisocyanate.—From 0.90 g. of *cis*-2-butene-1,4-diol and 1.72 g. of hexamethylene diisocyanate in mixed chlorobenzene–*o*-dichlorobenzene solvent there was obtained, after recrystallization from 90–10 methanol–dimethylformamide solution, 1.57 g. (60% yield) of polymer, m.p. 134–136°, inherent viscosity 0.12.

Anal. Calcd. for $C_{12}H_{20}N_2O_4$: C, 56.25; H, 7.85; N, 10.92. Found: C, 56.46; H, 7.93; N, 11.06.

Polyurethan from *trans*-2-Butene-1,4-diol and 1,6-Hexamethylene Diisocyanate.—From 0.943 g. of *trans*-2-butene-1,4-diol and 1.80 g. of hexamethylene diisocyanate there was obtained, upon purification, 2.065 g. of a polyurethan (75% yield), m.p. 175–177°, inherent viscosity 0.19.

Anal. Found: C, 56.33; H, 7.91; N, 10.67.

Mixed Polyurethans.—In the preparation of the 80–20 and 20–80 polyurethans, the general procedure was modified to ensure reaction of both glycols. A mixture of 20 parts each of the two glycols was allowed to react with 100 parts of the diisocyanate, after which the remaining 60 parts of the one glycol were then added. In all other respects the reaction was performed according to the usual procedure.

***cis* 20–80 Polyurethan.**—A mixture of 0.33 g. of butane-1,4-diol and 0.325 g. of *cis*-2-butene-1,4-diol was heated with 3.10 g. of hexamethylene diisocyanate, after which an additional 0.975 g. of *cis*-2-butene-1,4-diol was added and

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[8] N. Bekkedahl, *J. Research Natl. Bur. Standards*, **13**, 411 (1934).

[9] All melting points are corrected for stem exposure.

[10] A. W. Johnson, *J. Chem. Soc.*, 1014 (1946).

[11] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, New York, N. Y., 1940.

[12] C. Prevost and A. Lutz, *Compt. rend.*, **198**, 2264 (1934).

the reaction completed. After purification a polymer of m. p. 117–121°, inherent viscosity, 0.10 was obtained.

Anal. Calcd. for $C_{12}H_{20.4}N_2O_4$: C, 56.14; H, 7.97; N, 10.90. Found: C, 55.72; H, 7.74; N, 10.04.

cis **90–10 Polyurethan.**—This polymer was formulated to be 80–20, but even though the modified procedure for mixed polyurethans was used, the physical data indicate that the product is closer to 90–10. A mixture of 0.322 g. of *cis*-glycol and 0.332 g. of saturated glycol was allowed to react with 3.10 g. of hexamethylene diisocyanate, and then an additional 0.994 g. of butane-1,4-diol was added dropwise. Upon purification 4.25 g. (89% yield) of polymer was obtained, m. p. 168–170°, inherent viscosity 0.11.

Anal. Calcd. for $C_{12}H_{21.8}N_2O_4$: C, 55.83; H, 8.49; N, 10.86. Found: C, 56.22; H, 8.30; N, 10.73.

trans **20–80 Polyurethan.**—Under the modified procedure for mixed polyurethans, a polymer was prepared from a mixture of 0.955 g. of *trans*-2-butene-1,4-diol and 0.244 g. of butane-1,4-diol with 1.82 g. of hexamethylene diisocyanate. After recrystallization 2.08 g. (69% yield) of product was obtained, m. p. 155–157°, inherent viscosity 0.12.

Anal. Found: C, 56.04; H, 8.08; N, 10.53.

trans **80–20 Polyurethan.**—A mixture of 0.407 g. of *trans*-2-butene-1,4-diol and 1.667 g. of butane-1,4-diol was allowed to react with 3.89 g. of hexamethylene diisocyanate, according to the modified procedure. After purification of the crude product 5.06 g. (85% yield) of polymer was obtained, m. p. 160–162°, inherent viscosity 0.11.

Anal. Calcd. for $C_{12}H_{21.6}N_2O_4$: C, 55.88; H, 8.43; N, 10.86. Found: C, 55.76; H, 8.66; N, 10.57.

Polyesters.—The apparatus used was that described by Hardy.[13] The polyesters were prepared from sebacic acid and *cis*- or *trans*-2-butene-1,4-diol according to the procedure described for 2-butyne-1,4-diol polymers. A reaction temperature of 170° was maintained by refluxing phenetole vapors, and an oxygen-free nitrogen atmosphere was obtained at all times. The inherent viscosities were measured on a 0.4% solution of the polymer in chloroform.

Polysebacate of *cis*-2-Butene-1,4-diol.—From a mixture of 2.213 g. of *cis*-2-butene-1,4-diol and 4.620 g. of sebacic acid there was obtained, after purification, 5.75 g. (90% yield) of polymer, m. p. 58–59°, inherent viscosity 0.56.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.13; H, 8.72. Found: C, 65.98; H, 8.45.

Polysebacate of *trans*-2-Butene-1,4-diol.—A run made with 2.475 g. of *trans*-2-butene-1,4-diol and 5.160 g. of sebacic acid gave 6.15 g. (86% yield) of polymer, m. p. 68–69.5°, inherent viscosity 0.30.

Anal. Found: C, 65.86; H, 8.53.

Second Order Transition Temperature Determinations.—The method of Bekkedahl[8] was followed. Isoöctane was employed as the confining liquid and polymer samples of about 5 g. were used. The capillary scale readings were plotted against the temperature as measured by a thermocouple without determining absolute volume changes. Therefore, the measurements may be in error by a few degrees, but the general order of the values is undoubtedly correct.

Heat and Entropy of Fusion Calculations.—The melting points used were corrected capillary melting points and these may not represent the precise value for the disappearance of crystallinity. Also there is some difference in molecular weights of the samples as judged by their inherent viscosity, and this introduces a slight element of doubt on exact comparison, but the order of magnitude is the important point in this work.

Summary

cis-2-Butene-1,4-diol has been prepared by the Raney nickel-catalyzed hydrogenation of 2-butyne-1,4-diol.

The *cis* and *trans* isomers of 2-butene-1,4-diol have been converted to polyurethans by reaction with hexamethylene diisocyanate, and to polyesters by reaction with sebacic acid. The capillary melting points of the *cis* polymers are lower than the *trans* isomers, but second order transition temperatures, heat and entropy of fusion calculations, X-ray diffraction and infrared patterns show little difference attributable to *cis–trans* isomerism.

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(13) D. V. N. Hardy, *J. Soc. Chem. Ind.*, **67**, 426 (1948).

[CONTRIBUTION FROM THE MERCK INSTITUTE FOR THERAPEUTIC RESEARCH AND THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Vitamin B$_{12}$. XII. Vitamin B$_{12}$-like Activity of α- and β-Ribazole

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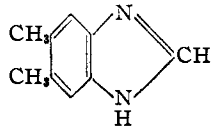
5,6-Dimethylbenzimidazole (I) has been obtained[1,2] as a degradation product of vitamin B$_{12}$. 1,2-Diamino-4,5-dimethylbenzene (II) may also be considered as a vitamin B$_{12}$ degradation product, since it was obtained as a dibenzoyl derivative[1] by further degradation of 5,6-dimethylbenzimidazole.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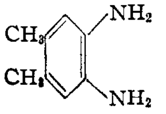
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It was considered significant to determine whether small fundamental units of vitamin B$_{12}$, which is a compound having a molecular weight of approximately 1300,[3] would possess vitamin B$_{12}$-like activity or APF (animal protein factor) activity. The tests for activity were made by assays on rats which were maintained on a diet devoid of animal protein and containing 0.25% of thyroid powder; it was known that the addition of vitamin B$_{12}$ to this diet counteracted the growth retarding effect of the thyroid powder, and caused a marked increase in the weight gain of the animals.[4]

Daily doses of 2–5 mg. of 5,6-dimethylbenzimidazole or 2–3 mg. of 1,2-diamino-4,5-dimethylbenzene caused weight gains which were comparable to the growth produced by the addition of 0.125–0.25 μg. of vitamin B$_{12}$. Thus, 5,6-dimethylbenzimidazole and 1,2-diamino-4,5-dimethylbenzene show vitamin B$_{12}$-like activity in this test.[5] Even

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(1) Brink and Folkers, THIS JOURNAL, **71**, 2951 (1949).

(2) Holliday and Petrow, *J. Pharm. and Pharmacol.*, **1**, 734 (1949); Beavan, Holliday, Johnson, Ellis, Mamalis, Petrow and Sturgeen, *ibid.*, **1**, 957 (1949).

(3) Brink, Wolf, Kaczka, Rickes, Koniuszy, Wood and Folkers, THIS JOURNAL, **71**, 1854 (1949).

(4) Emerson, *Proc. Soc. Exp. Biol. Med.*, **70**, 392 (1949).

(5) Emerson, Brink, Holly, Koniuszy, Heyl and Folkers, THIS JOURNAL, **72**, 3084 (1950).