

MOLECULAR STRUCTURE OF $B_{10}H_{12}(CH_3CN)_2$

Sir:

Decaborane reacts with acetonitrile to form¹ a substitution derivative, $B_{10}H_{12}(CH_3CN)_2$, in which a covalent bond has been tentatively assumed¹ between the CH_3CN groups. On the other hand, our results indicate, somewhat surprisingly, that the CH_3CN groups are linear and are each attached by a single N-B bond, and that they are not attached to each other.

The molecular structure, shown in Fig. 1, is based on the boron arrangement in decaborane. The heavy atoms were located from the Patterson function calculated from 956 X-ray diffraction maxima obtained from a single crystal. The hydrogen atom positions, except for those of the methyl groups, were uniquely established from difference electron density maps.

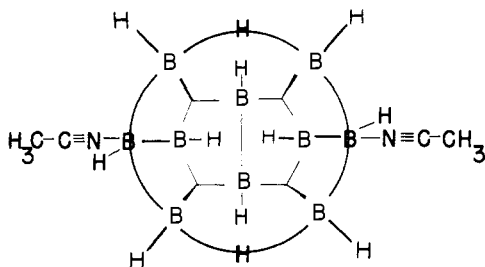


Fig. 1.—Topological drawing of the $B_{10}H_{12}(CH_3CN)_2$ structure showing the three-center bond approximation to the valence theory. The isolated molecule apparently has C_{2v} symmetry, which has been distorted here for clarity in the case of two hydrogen atoms. Regarded as a derivative of $B_{10}H_{14}^{-2}$, the boron-hydrogen arrangement has the 2632 topology,³ with two bridge hydrogen atoms. Bond distances are within normal ranges.

Unit cell values are $a = 7.81$, $b = 11.31$, $c = 14.18$ and $\beta = 96^\circ 52'$. The space group of $I2/c$ requires that the molecule shall have at least a twofold axis. Refinement, still in progress, has reached the values of $R = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|} = 0.17$ and $r = \frac{\sum w(F_0^2 - F_c^2)}{\sum wF_0^4} = 0.20$ for all observed reflections.

The structure has interesting chemical implications. First, it is to be regarded as a substitution derivative of $B_{10}H_{14}^{-2}$, not of $B_{10}H_{14}$. This ion has been suggested on the basis of valence theory²; its negative charge probably can best be accommodated by transformation from the 4450 topology² to either the 2632 or 0814 structures.³ Second, it suggests that these two particular boron atoms (Fig. 1), presumably most positive in $B_{10}H_{14}$ because of abstraction of negative charge by the two bridge hydrogens, are most susceptible to substitutional attack by an electron donor.

We wish to thank Professor Riley Schaeffer for supplying us with single crystals. We are greatly indebted to Dr. F. L. Hirshfeld, who took many of the diffraction photographs. For financial support

(1) R. Schaeffer, *THIS JOURNAL*, **79**, 1006 (1957).

(2) W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958). See also R. H. Toeniskoetter, G. W. Schaeffer, E. C. Evers and G. E. Bagley, Abstracts of 134th Meeting, A.C.S., Chicago, Ill., Sept. 7-12, 1958, p. 23-4.

(3) W. N. Lipscomb, *Advances in Inorganic and Radiochemistry*, Academic Press, Inc., New York, N. Y., Vol. I, 1959, p. 146.

we wish to thank the Office of Naval Research, the Office of Ordnance Research and the Shell Development Company. The fourteen hours of computing time on the UNIVAC SCIENTIFIC 1103 were contributed in part by the University of Minnesota.

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THE ENZYMIC CONVERSION OF MEVALONIC ACID-2-C¹⁴ TO AN OLEFINIC ACID¹

Sir:

Although 3,5-dihydroxy-3-methylpentanoic acid (mevalonic acid, MVA) has been demonstrated to be a very efficient precursor of squalene^{2,3} and cholesterol⁴ in animal tissues, the identity of dimeric or trimeric intermediates between mevalonic acid and squalene has not been elucidated. We now wish to report the isolation and probable structure of a long-chain olefinic acid which accumulates as a metabolite of MVA in rat liver.

As shown in Table I, the conversion of MVA-2-C¹⁴ to non-saponifiable lipids requires both the high speed supernatant fraction of rat liver and the microsomes. The omission of microsomes leads to the accumulation of a petroleum ether extractable C¹⁴-labeled olefinic acid. The cofactor requirements for both of these conversions were found to be quite similar. Therefore, it seems reasonable to suppose that the long-chain olefinic acid is either an intermediate in squalene biosynthesis or is closely related structurally to an intermediate.

TABLE I

THE INCORPORATION OF MEVALONIC ACID-2-C¹⁴ INTO AN OLEFINIC ACID

	Total c./m. in acidic fraction	Total c./m. in non-acidic fraction	Total c./m. in non-saponifiable lipid
Soluble enzyme preparation ^a	1140	183	
Soluble enzyme preparation plus microsomes		30	1010

^a The soluble enzyme preparation consisted of the supernatant fraction after the centrifugation of a rat liver homogenate at $78,410 \times g$ for two hours.

A large-scale incubation of MVA-2-C¹⁴ (S.A. 3,378 c./m./mg.) with the soluble enzyme preparation led to the isolation of 5 mg. of the unsaturated acid (S.A. 5,353 c./m./mg.). The greater specific activity of the unsaturated acid as compared with the original MVA would indicate that MVA was the sole precursor and that it was converted in a net manner with a loss of some portion of the MVA molecule during conversion. The equivalent weight of this acid was found to be 292. Both the specific activity and the equivalent weight would indicate that the acid was only 90% pure based on the proposed structure presented later.⁵

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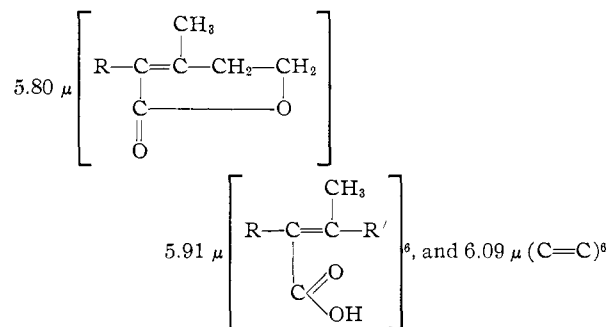
(2) J. W. Cornforth, R. H. Cornforth, G. Popjak and I. Youhotsky-Gore, *Biochem. J.*, **66**, 10P (1957).

(3) F. Dituri, S. Gurin and J. L. Rabinowitz, *THIS JOURNAL*, **79**, 2650 (1957).

(4) P. A. Tavormina, M. H. Gibbs and J. W. Huff, *ibid.*, **78**, 4498 (1956).

(5) See J. W. Ogilvie, Jr., *THIS JOURNAL*, **81**, 756 (1959).

The methyl ester was prepared, purified by vapor phase chromatography, and found to have an absorption maximum at 228 m μ . The infrared spectrum of the acid was characterized by three absorption maxima in the 5 to 7 μ region. These maxima and their tentative assignments are



The acid when chromatographed on filter paper in an ethanol-ammonia system⁷ migrated as a single spot and had an R_f of 0.75. This spot could be detected by its radioactivity, by spraying with brom thymol blue, or by the decolorization of KMnO_4 .

Preliminary experiments have indicated that the isolated acid is rather poorly converted to non-saponifiable lipids by rat liver homogenates. It seems possible that the acid may exist in an activated form prior to isolation or that some minor structural modification, such as a double bond migration, may have occurred during the isolation and purification procedures.

The structure of the isolated acid has been determined and is reported in the following communication.⁵

(6) J. Cason, N. K. Freeman and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951).

(7) E. P. Kennedy and H. A. Barker, *Anal. Chem.*, **23**, 1033 (1951).

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CRYSTAL STRUCTURES OF NICKEL AND PALLADIUM DIMETHYLGLYOXIMES¹

Sir:

Both palladium and nickel dimethylglyoximes (PdDMG and NiDMG) crystallize in the space group I_{bam} and are nearly isostructural. For NiDMG the intensity data of Godycki² were used for least squares refinement on the IBM 650 computer. The nickel scattering factor was corrected for anomalous dispersion.³ Intensity data from the $[hk0]$ and $[hkl]$ planes of PdDMG were taken with a Norelco proportional counter using copper radiation. Details of the structure determination have been given previously.¹ Values of the atomic parameters and of the reliability index, R , for the two structures are given in Table I, which lists the intramolecular distances and their standard deviations. The lattice constants are $a = 16.68$ and 16.85 ,

(1) Contribution No. 698. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

(3) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

$b = 10.44$ and 10.49 , and $c = 6.49$ and 6.52 Å. for NiDMG and PdDMG, respectively.

TABLE I

ATOMIC PARAMETERS

Atom	Parameter	NiDMG	Std. dev.	PdDMG	Std. dev.
O _I	x	0.1577	0.0009	0.1618	0.0012
	y	.0991	.0014	.0960	.0020
O _{II}	x	.0543	.0009	.0500	.0012
	y	.2589	.0015	.2654	.0021
N _I	x	.1111	.0009	.1179	.0013
	y	.9931	.0019	.9901	.0025
N _{II}	x	.9909	.0011	.9868	.0014
	y	.1765	.0014	.1829	.0022
C _I	x	.0808	.0013	.0864	.0017
	y	.7741	.0022	.7744	.0028
C _{II}	x	.1440	.0013	.1471	.0018
	y	.8813	.0020	.8748	.0028
C _{III}	x	.0988	.0015	.1076	.0019
	y	.6334	.0024	.6305	.0031
C _{IV}	x	.2348	.0015	.2373	.0020
	y	.8575	.0023	.8522	.0031
R		.124		.065	

$$R = \frac{\sum |F_0| - |F|}{\sum |F_0|}$$

TABLE II

INTRAMOLECULAR DISTANCES (Å).

Distance	NiDMG	Std. dev.	PdDMG	Std. dev.
M-N _I	1.85	0.015	1.99	0.020
M-N _{II}	1.85	.015	1.93	.021
O _I -O _{II}	2.40	.021	2.59	.030
O _I -N _I	1.35	.023	1.33	.031
O _{II} -N _{II}	1.36	.023	1.37	.031
N _I -C _{II}	1.29	.028	1.31	.038
N _{II} -C _I	1.30	.028	1.31	.037
C _I -C _{II}	1.54	.031	1.47	.041
C _I -C _{III}	1.50	.033	1.55	.044
C _{II} -C _{IV}	1.53	.033	1.54	.045

The PdDMG molecule appears to be less symmetrical than the NiDMG molecule. The two crystallographically different Pd-N and N-O distances differ from each other; the difference appears to be significant for the Pd-N distances. The hydrogen bonded O-O distance in PdDMG is also significantly greater than the corresponding distance in NiDMG. The observed difference in symmetry would be the expected result if NiDMG possessed a symmetrical hydrogen bond and PdDMG an unsymmetrical one, leading to non-equivalence of N-O and Pd-N distances in the latter. It has been estimated by Huggins⁴ that at hydrogen bonded O-O distances of 2.65 Å. and below, the hydrogen bond should become symmetrical. This work, as well as recent neutron diffraction results,⁵ indicates that Huggins' critical distance is perhaps somewhat high, but does support the thesis of a single potential minimum below a certain O-O distance, and suggests that this limit has been reached in NiDMG.

On the basis of the observed O-O distance, the empirical correlation of Nakamoto, Margoshes

(4) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

(5) G. E. Bacon and R. S. Pease, *Proc. Roy. Soc. (London)*, **A230**, 359 (1955).