

means of a study of the simpler component systems. However, even allowing for slight differences due to the effect of the sodium present in this investigation, only poor agreement was found between the results of this research and Malquori's published data. A review of Malquori's results was commenced, but this is still incomplete. However, it may be pointed out that a preliminary investigation of the system $\text{AlCl}_3\text{-HCl-H}_2\text{O}$ at 25° gave results which differed widely from those of Malquori. For example, fair agreement was found with the value for the solubility of aluminum chloride hexahydrate in water, given by Ehret and Frere,⁵ of 31.10%. Seidell⁶ quotes 31.6% as an average value. On the other hand, Malquori's curves for the solubility of aluminum chloride in this system are based on the value 34.08%, which is almost cer-

(5) W. Ehret and G. Frere, *THIS JOURNAL*, **67**, 68 (1945).

(6) A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," 3rd ed., Vol. 1, p. 83.

tainly about 10% higher than the correct value.

Acknowledgments.—The writer acknowledges the collaboration of Mr. W. E. Ewers, of the C. S. I. R. in the preliminary phase rule investigation; and of Professor N. S. Bayliss, under whose supervision this work was carried out. He also wishes to thank Western Australian Industries Department for permission to publish these results.

Summary

A limited study has been made of the system $\text{AlCl}_3\text{-FeCl}_3\text{-KCl-NaCl-HCl-H}_2\text{O}$ at 25, 30 and 35° , in solutions saturated with aluminum chloride and sodium chloride, with special reference to the composition of solutions in equilibrium with both solid potassium chloride and the double salt $2\text{KCl}\cdot\text{FeCl}_3\cdot\text{H}_2\text{O}$.

UNIVERSITY OF WESTERN AUSTRALIA

PERTH, W. A.

RECEIVED JUNE 26, 1946

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY OF THE IOWA STATE COLLEGE]

The Structure of Uranium Hydride and Deuteride¹

BY R. E. RUNDLE

Uranium metal reacts with hydrogen to form only one hydride. This hydride, established as a compound by X-ray diffraction,² has been found chemically to have the composition UH_3 .³

The hydride of uranium, if existing data on other metallic hydrides be reliable, is unique in that it does not fall in the class of volatile hydrides, salt-like hydrides or interstitial solution hydrides. It is a metal-like hydride of perfectly definite composition, and with a structure completely unrelated to any of the three forms of uranium metal. It has a structure in which the bonding between uranium and hydrogen must play a predominant role, since metal-metal bonds of any strength are almost completely lacking.

Unit Cell and X-Ray Density.—Debye-Scherrer powder diagrams of uranium hydride have been made using $\text{CuK}\alpha$ radiation, a camera of 5-cm. radius, and samples sealed in thin-walled glass capillaries. These diagrams may be interpreted in terms of a primitive cubic lattice, $a = 6.63 \text{ \AA}$. The density of the hydride has been measured by helium displacement and found to

be 10.95 g./cc.⁴ There are then eight uranium atoms in the cubic unit.

A precise determination of the unit cell has been made using a symmetrical, self-focusing powder camera of 5-cm. radius and unfiltered $\text{CuK}\alpha$ radiation. Samples were prepared from purest Ames uranium and carefully purified hydrogen (purified by decomposition of uranium hydride).⁵ The samples of Table I were prepared at about 1-atm. hydrogen pressure and at relatively low ($200\text{--}300^\circ$) temperatures. Due to small particle size these samples produced satisfactory but not particularly sharp reflections in the back reflection region.

Other samples, prepared by W. Tucker and P. Figard, were made at pressures up to 1800 p.s.i. and temperatures up to $500\text{--}600^\circ$. These samples showed considerable growth in particle size and produced very sharp maxima in the back reflection region. The lattice spacing, as determined from these samples (Table II), is more precise but within the limit of experimental error of the spacing of the low pressure hydride.

Uranium metal has been heated with uranium hydride, and two phases are maintained. Changes in spacing of neither uranium metal nor of hydride were great enough to be detected. For example, a sample 50% uranium metal and 50%

(1) Paper No. 10 of the Institute for Atomic Research. Work done under Contract W-7405 eng-82, Manhattan District, U. S. Corps of Engineers. F. H. Spedding, Project Director. The information covered in this document will appear in Division VIII of the Manhattan Project Technical Series.

(2) R. Rundle, Metallurgical Project Report, CT-609, p. 30, April (1943).

(3) Battelle Memorial Institute, Metallurgical Project Report, CT-818, July, 1943. Other physical and chemical reports on the hydride will be made in *THIS JOURNAL* by F. Spedding, A. Newton, J. Warf, *et al.*

(4) A. Newton, J. Warf, O. Johnson and R. Nottorf, Metallurgical Project Report CC-1201, Jan. (1944).

(5) This method of purification, first described by A. Newton, has been shown to be very effective.⁴

uranium hydride gave a hydride spacing of $6.630 \pm 0.002 \text{ \AA}$.

Neither hydrides prepared at high hydrogen pressures nor hydrides prepared with excesses of metal showed any alteration in the uranium hydride spacing. It must be concluded that the composition of uranium hydride is perfectly definite, that there is no appreciable solubility of hydrogen or uranium in the hydride at ordinary temperatures and pressures.

TABLE I

LATTICE CONSTANT OF URANIUM HYDRIDE PREPARED AT LOW PRESSURE

	No. of lines	Spacing, \AA .	Estimated error (one film)
Sample I	8	6.6323	± 0.0010
Sample I ^a	6	6.6324	.0009

^a Measured by another observer.

TABLE II

LATTICE CONSTANT OF URANIUM HYDRIDE PREPARED AT 1800 P.S.I. HYDROGEN

Sample	No. lines	Spacing, \AA .	Estimated error (one film)
A	12	6.6308	± 0.0008
B	12	6.6317	.0008
C	12	6.6312	.0005
D	12	6.6319	.0008
E	19	6.6306	.0008
A ^a	12	6.6302	.0014
B ^a	12	6.6304	.0009
C ^a	12	6.6301	.0017
D ^a	12	6.6317	.0011

^a Measured by another observer.

We consider the best value of the hydride spacing to be $6.6310 \pm 0.0008 \text{ \AA}$. The X-ray density calculated in accordance with the recommendations of Jette and Foote,⁶ is 10.92 g./cc., in excellent agreement with the experimental value obtained by helium displacement.⁴

Lattice Constant of the Deuteride.—The deuteride, UD_3 , has been prepared at low pressures. Precision diagrams, taken as before with $\text{CuK}\alpha$ radiation, lead to a lattice constant, $a = 6.620 \pm .002 \text{ \AA}$, more than 0.01 \AA smaller than the

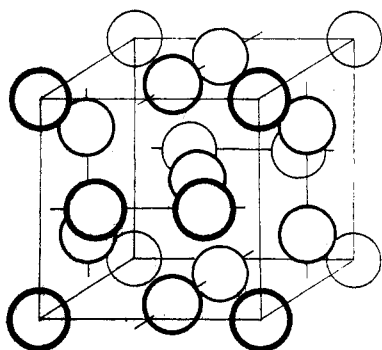


Fig. 1.—Uranium positions in the hydride.

(6) E. Jette and F. Foote, *J. Chem. Phys.*, **3**, 605 (1935).

hydride spacing. This change in lattice constant is far greater than the experimental error. The X-ray density of the deuteride is 11.11 g./cc.

Space Group and Structure.²—Powder diagrams of uranium hydride show many absences. These absences, which persist even on the most intense powder diagrams, seem to be systematic and most extraordinary. They include reflections with the following forms of Miller indices

$$(4n, 4n' + 2, 4n'' + 2); (4n, 4n', 4n'' + 2); (4n + 2, 4n' + 2, 2n'' + 1); (2n + 1, 2n' + 1, 2n'' + 1); (4n, 2n' + 1, 2n'' + 1)$$

All other possible reflections have been observed with good intensity on powder diagrams made with $\text{CuK}\alpha$ radiation.

The above absences correspond to no special set of equivalent positions in the cubic system, and it can be shown that no set of eight equivalent uranium atoms with any parameters in any space group will lead to these absences. The same can be shown for any two sets of four equivalent positions for the uranium atoms.

The space groups O_h^3 , O^2 and T_d^4 provide two equivalent positions plus six equivalent positions which combined lead to a structure which requires the above noted absences and no others. These positions are: two atoms in (a) at 000 , $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and six atoms in (c) at $\frac{1}{4}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{4}0$, $0\frac{1}{4}\frac{1}{2}$, $\frac{3}{4}0\frac{1}{2}$, $0\frac{3}{4}\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}0$ (or the six equivalent positions may be taken $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ from the above).

The parameterless structure provides good agreement between observed and calculated intensities (Table III). The observed intensities were visually estimated from powder diagrams. Calculated intensities were corrected for Lorentz, polarization and multiplicity factors. No absorption correction nor temperature correction was made, so that the ratio of calculated and observed intensities changes with angle, but in a regular fashion. The absences noted demand the parameterless structure within very narrow limits, so it seems unnecessary to carry the intensity calculations further.

Discussion of the Structure.—The metal positions of uranium hydride are shown in Fig. 1. The atoms in the six equivalent positions, (c), form three perpendicular but non-intersecting linear arrays of atoms running parallel to the three cubic axes. The atoms are spaced at half the cube edge, or at 3.316 \AA ; each (c) atom possesses two other (c) atoms as nearest neighbors at this distance. This is by far the shortest metal-metal bond in the compound, and apparently is the only metal-metal bond of any strength in the structure.

In addition, each (c) atom has four nearest (a) atoms as neighbors at 3.707 \AA . These neighbors form a tetrahedron flattened out along one two-fold axis. Each (a) atom has twelve nearest neighbors, (c), at 3.707 \AA . These twelve neighbors have the arrangement of a deformed icosahedron.

TABLE III
INTENSITIES OF POWDER REFLECTIONS FROM URANIUM
HYDRIDE

Indices	Intensity calculated	Intensity observed ^a
(100)	0	0
(110)	0	0
(111)	0	0
(200)	1427	W
(210)	4147	S
(211)	3274	MS
(220)	0	0
(300) (221)	0	0
(310)	0	0
(311)	0	0
(222)	416	W
(320)	1068	M
(321)	1889	VS
(400)	772	M
(410) (322)	0	0
(411) (330)	0	0
(331)	0	0
(420)	524	MW
(421)	964	MS
(332)	451	MW
(422)	0	0
(500) (430)	0	0
(510) (431)	0	0
(511) (333)	0	0
(520) (432)	855	S
(521)	538	MS
(440)	506	MS
(522) (441)	0	0
(530) (433)	0	0
(531)	0	0
(600) (442)	270	MW
(610)	208	W
(611) (532)	605	MS
(620)	0	0
(621) (540) (443)	0	0
(541)	0	0
(533)	0	0
(622)	175	W
(630) (542)	544	MS
(631)	349	M
(444)	233	MW
(700) (632)	0	0
(710) (550) (543)	0	0
(711) (551)	0	0
(640)	180	W
(720) (641)	558	MS
(721) (633) (552)	714	S
(642)	0	0
(722) (544)	0	0
(730)	0	0
(731) (553)	0	0
(650) (643)	646	S
(732) (651)	905	VS
(800)	237	W
(810) (740) (652)	0	0
(811) (741) (554)	0	0
(733)	0	0

^a S = strong; M = medium; W = weak; V = very.

The metal-metal distances are known in the α and γ (high temperature) forms of uranium. In the former,⁷ each metal atom has two neighbors at 2.76 Å., two at 2.85 Å., four at 3.27 Å. and four at 3.36 Å. In the body-centered, γ form of the metal, each metal atom has eight nearest neighbors at 2.97 Å.⁸ Accordingly, the 3.316 Å. spacing in the hydride represents metal-metal bonds of a strength corresponding to the weaker bonds in the α -metal structure. Since there are but two such bonds per (c) atom and none for the (a) atoms, the metal-metal bonding in uranium hydride is relatively unimportant. This might also be concluded from the density which decreases from 19 to about 11 on formation of the hydride.

In no sense of the word can uranium hydride be thought of as an interstitial solution. Its composition is definite, the metal arrangement unique and unrelated to that of any metal structure, and metal-metal bonds are practically non-existent in this hydride.

In the absence of structural data, however, uranium hydride would doubtless be listed as an interstitial solution, since in appearance and conductivity it still resembles a metal.

A Proposal Concerning the Nature of the Hydride.—As we have seen, the metallic properties of uranium hydride are quite inconsistent with an ionic structure, and the chemical and physical properties and the structure of the hydride do not correspond to an interstitial solution. The lack of important metal-metal bonds suggests that the important bonds in the structure are metal-hydrogen bonds, and these bonds must be such as to leave the structure with metallic properties.

Moreover, though the melting point of the hydride is unknown it is certainly fairly high for a compound with such weak metal-metal bonds. At high hydrogen pressures the hydride has been taken above 600°, and it is certain that the melting point is much higher. In addition, since the metal breaks up into a powder on formation of the hydride it must be that the hydride is brittle. The particles of the hydride produced at high temperatures were large enough to confirm this property.

The properties cited above certainly must mean that covalent bonding of hydrogen to individual uranium atoms, leading to a molecular crystal, is out of the question. It is also inconsistent with the two very different types of uranium atoms in the structure.

The physical properties of the hydride, such as melting point and brittleness, are in keeping with a valence-type compound, *i. e.*, a continuous structure held together by covalent bonds.⁹

(7) C. Jacobs and B. Warren, *THIS JOURNAL*, **59**, 2588 (1937).

(8) A. Wilson and R. Rundle, Metallurgical Project Report, CT-1775, May (1944): Apparently γ -uranium was obtained by chance earlier. See J. McLennan and R. McKay, *Trans. Roy. Soc. Canada*, III, **24**, 1, (1930).

(9) This terminology follows that of F. Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940, Chapt. I.

Since metal-metal bonds are absent or weak, the continuous structure can be provided only by metal-hydrogen bonds, and by these only if hydrogen bridges metal atom to metal atom.

To provide electrical conductivity it is also necessary to have a continuous structure. Without good metal-metal bonds this, too, can only be provided by a metal-hydrogen-metal bridge structure.

Finally, the nearest metal-metal distances in the hydride are, except for the 3.316 Å. spacing, too long to be metal-metal bonds and too short to provide space for hydrogen between metal atoms except in a bridge-type structure. Indeed if one tries to find sensible places for hydrogen without the use of a bridge structure the uranium hydride structure appears incomprehensible.

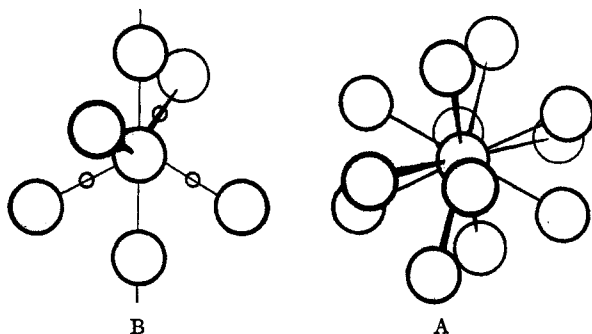


Fig. 2.—Coordination about uranium atoms in the hydride. (A) Twelve nearest neighbors (c) about uranium atom (a). All twelve distances are equal (3.707 Å.) and the (c) atoms lie at the corners of a nearly regular icosahedron. In accordance with the proposal presented in the paper, each of twelve bonds is an U-H-U bridge. (B) Two nearest (c) atoms (3.316 Å.) and four nearest (a) atoms (3.707 Å.) about any (c) atom. The shorter bond is an ordinary U-U bond and the longer bond is a U-H-U bridge, according to the proposal of this paper. The hydrogen atom is shown in the longer bond in this case.

The structure can be understood in terms of electron deficient "half bonds" of the type recently proposed to explain the bonding in the boron hydrides, aluminum alkyl dimers¹⁰ and certain interstitial carbides, nitrides and metallic oxides.¹¹ In accordance with this proposal, hydrogen may use its 1s-orbital for the formation of two bonds (but with one electron pair for the two bonds).^{12a} Since s-orbitals lack directional properties, we should expect the U-H-U¹² bond angle to be 180° because of the small size of hydrogen. Circumstances under which electron deficient "half bonds" are to be expected are described elsewhere.^{10,11} In this case we should expect them if

(10) R. Rundle, *THIS JOURNAL*, **69**, 1327 (1947).

(11) R. Rundle, "A New Interpretation of Interstitial Compounds," to be submitted for publication in *THIS JOURNAL*.

(12a) It has been called to my attention that a similar proposal was made by Longuet-Higgins and Bell, *J. Chem. Soc.*, 250 (1943).

(12) The bond should be drawn directly through hydrogen to indicate one electron pair, since U-H-U would normally imply two electron-pair bonds.

uranium has fewer valence electrons than stable bond-orbitals. That this condition is reasonable for uranium hydride we shall attempt to demonstrate below.

If we now consider which bonds in the structure must be the bridge bonds, U-H-U, the result is quite simple. The 3.316 Å. distance, as we have seen, corresponds to a metal-metal bond. The 3.707 Å. spacing is quite satisfactory for the bridge bonds, and all other distances are too large for such bonds. There are 12 such bridge bonds to each uranium atom of the set (a), or 24 per unit cell. There are then 24 hydrogens per unit cell, making the over-all formula UH₃.

In the structure proposed here each atom of type (a) is bonded to twelve atoms of type (c) by hydrogen bridges. Each atom of type (c) is bonded directly to two other type (c) atoms and by hydrogen bridges to four atoms of type (a).

This structure is consistent with the use of six orbitals of uranium for bond formation for both types of uranium atoms in the structure. The configuration about (c) uranium atoms is that of a tetrahedron flattened along one two-fold axis and with two extra bonds directed along the shortened two-fold axis. There are twelve bonds from type (a) atoms. These bonds are directed toward the corners of a nearly regular icosahedron, (see Fig. 2). If (a) type atoms use but six bond orbitals then they must use orbitals which are directed in two directions, and must use each orbital to form two "half bonds." If this is the case it is understandable that the six orbitals chosen for bond formation by the two types of atoms are unlike. If uranium can furnish at least six stable bond-orbitals and will furnish at most four valence electrons in hydride formation, which seems reasonable, then conditions for "half bonds" are fulfilled.

Of course, the structure is not entirely clarified by the proposal made here. The types of orbitals used for bond formation by uranium are not clear in case of either (a) or (c) type atoms. If, as Pauling has suggested,¹³ when uranium furnishes four valence electrons the 7s-orbital contains an electron pair, then the orbitals available for bond formation are the five 6d-orbitals, the three *p*-orbitals and quite possibly the 5f-orbitals.¹⁴ To obtain better bonding it would doubtless be possible to shift the electrons from the 7s-orbital to other almost equally stable levels. The best six hybrid bond-orbitals available to uranium are difficult to obtain from the wealth of atomic orbitals available. This is a problem beyond the scope of the proposal made here, and that it is difficult to solve is not a detraction from the present proposal.

The proposed structure provides uranium hydride with a continuous, valence-type bonding

(13) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 413.

(14) The elements in this part of the periodic table have rare-earth-like properties, suggesting the stability of the 5f-orbitals. See, for example, *Chem. Eng. News*, **24**, 161 (1946).

(Fig. 2) which will account for high melting point and brittleness, and with a resonating system of "half bonds" which should lead to high polarizability, metallic luster and high electrical conductivity, much as these properties are found in graphite. Moreover, it provides a satisfactory explanation for the uranium-uranium distances in the hydride and suggests satisfactory positions for precisely the correct number of hydrogen atoms.

The author is quite aware that it is impossible to defend the proposed structure except insofar as the proposal provides an explanation of the unusual properties, composition and metal arrangement of the hydride. This proposal is offered here because it seems unlikely that an M-H-M bridge is unique to uranium hydride. Many other metallic hydrides have rather similar properties, and though structural information is not yet complete enough to cite another good example of this type, it seems to the author that most "interstitial solution" compounds need further study. Nearly all such compounds, including hydrides, are brittle, hard and high melting, properties quite inconsistent with the weakening of metal-metal bonds unless replaced with better bonds. A number of metallic hydrides fulfill the conditions for "half bonds" as described before.¹¹

Acknowledgments.—The author wishes to express his appreciation to the members of the

Ames section of the Metallurgical Project for both samples and analytical data. Especial thanks are due Mr. A. S. Wilson for aid in the precise determination of hydride and deuteride spacings, to Mr. R. Nottorf, Dr. A. Newton, Messrs. W. Tucker and P. Figard for special sample preparations and to Drs. I. B. Johns and F. H. Spedding.

Summary

Uranium forms a metallic hydride, UH_3 , a compound of definite composition, unique metal arrangement unrelated to that of the metal itself, and almost lacking in metal-metal bonds.

The hydride is cubic, $a = 6.631 \text{ \AA}$., with eight uranium atoms per unit cell at positions (a) 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and (c) $\frac{1}{4}\frac{1}{4}0$, $0\frac{1}{4}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}0$, $0\frac{3}{4}\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$ of the space group O_h^3 , O^2 or T_d^4 . The X-ray density is 10.92 g./cc. The deuteride spacing is 6.620 \AA ., definitely smaller than for the hydride.

It is proposed that the hydrogens form uranium-hydrogen-uranium bridges between metal atoms of type (a) and (c) in the structure, where the bridge contains one electron pair for the two bonds. This structure accounts for the physical properties, unique metal arrangement and formula of the hydride, and is consistent with a recently proposed theory of electron deficient structures.^{10,11}

AMES, IOWA

RECEIVED FEBRUARY 21, 1947

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Synthesis of Chromium Hexacarbonyl^{1,2}

BY BENTON B. OWEN, JAMES ENGLISH, JR., HAROLD G. CASSIDY AND CLARISSA VANDERBILT DUNDON

Although satisfactory methods have been recorded³ for the preparation of tungsten hexacarbonyl and molybdenum hexacarbonyl by reaction of the metals, or their salts, with carbon monoxide in the presence of reducing agents, no practical synthesis of chromium hexacarbonyl has been published. Job and Cassal⁴ prepared small amounts of chromium hexacarbonyl from phenylmagnesium bromide and chromic chloride in the presence of carbon monoxide at atmospheric pressure. They obtained yields of 14% or less, and this unsatisfactory conversion was confirmed by others.^{5,6} Recently, Anissimov and Nesmeyanov⁷

carried out this same reaction at 115 atm. and reported yields as high as 22%. Our interest in this synthesis arose from an immediate need for a supply of chromium carbonyl for research purposes. Our efforts were therefore directed toward increasing the yields obtained by known methods rather than toward discovering new reactions or investigating the mechanism of old ones. In the following section we outline the procedures by which we obtained the highest yields (67% at 50 atm., and 24% at 1 atm.) by the action of carbon monoxide upon phenylmagnesium bromide and chromic chloride. In the final section we discuss results which might be of interest in a further study of the peculiar chemistry of organic chromium compounds.

Experimental

Materials.—The chromic chloride was a commercial product dried at 250° in nitrogen and screened to 40 mesh. Moisture in this material had no deleterious effect other than consumption of Grignard reagent.

All yields were calculated on the basis of per cent. of an-

(1) Published with the permission of C. L. Lee, Captain U.S.N., for the Navy Department, and R. B. Douless, Major CAC, for the War Department.

(2) Abstracted from NDRC Report No. A-401, the first of two final reports covering the work done at Yale University under Contract OEMsr-1318 for Division One of the National Defense Research Committee, L. H. Adams, Chief.

(3) I. G. Farbenindustrie A. G., Patents; *Chem. Zentr.*, **102**, II, 2041 (1931); **103**, I, 2498, 2753 (1932).

(4) A. Job and A. Cassal, *Compt. rend.*, **183**, 392 (1926).

(5) W. Hieber and E. Romberg, *Z. anorg. allgem. Chem.*, **221**, 321 (1935).

(6) M. Windsor and A. Blanchard, *This Journal*, **56**, 823 (1934).

(7) K. N. Anissimov and A. N. Nesmeyanov, *Compt. rend. acad. sci. U. R. S. S.*, **26**, 58 (1940).