

## The Crystal Structure of Hydrazinium Dichloride, $\text{N}_2\text{H}_6\text{Cl}_2$

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Citation: *The Journal of Chemical Physics* **15**, 115 (1947); doi: 10.1063/1.1746438

View online: <http://dx.doi.org/10.1063/1.1746438>

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# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 15, NUMBER 3

MARCH, 1947

## The Crystal Structure of Hydrazinium Dichloride, $N_2H_6Cl_2$ \*

JERRY DONOHUE† AND WILLIAM N. LIPSCOMB‡

*Department of Chemistry, California Institute of Technology, Pasadena, California*

(Received December 31, 1946)

Accurate values of the two parameters in the structure of crystalline hydrazinium dichloride have been determined by the x-ray diffraction method, with the use of one and two dimensional Fourier syntheses. The N—N separation in this crystal is 1.42Å, and is equal to that in hydrazinium difluoride. This N—N distance is 0.05Å shorter than in gaseous hydrazine. Each chloride ion forms hydrogen bonds with three nitrogen atoms, the structure consisting of a three dimensional network of N—H···Cl bonds. The angle N—N—H···Cl is 100°. The configuration of the  $N_2H_6^{++}$  ions is *trans*. The differences between this structure and that of hydrazinium difluoride probably arise from the greater coordinating ability of the chloride ion as compared with that of the fluoride ion. The shortening of the N—N distance may be caused in part by the formal charges on the nitrogen atoms, although it seems certain that this formal charge effect is not of general validity.

THE crystal structure of hydrazinium dichloride was first investigated by Wyckoff,<sup>1</sup> who found that crystals of the substance belong to the space group  $T_h^6-Pa3$ , and that four molecules of  $N_2H_6Cl_2$  are situated in the unit cube, with  $a_0 = 7.89$ Å. Wyckoff, with the methods then available, was able to arrive at only approximate values of the two parameters necessary to determine the structure completely (excluding the hydrogen atoms). He described the structure as "a  $CaF_2$  grouping in which the chlorine ions are displaced from the symmetrical  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$  positions by the dumb-bell shaped  $N_2H_6$  groups."<sup>2</sup>

\* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1109.

† Predoctoral Fellow of the National Research Council.

‡ Present address: School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.

<sup>1</sup> R. W. G. Wyckoff, *Am. J. Sci.* 5, 15 (1923).

<sup>2</sup> R. W. G. Wyckoff, *The Structure of Crystals* (Reinhold Publishing Company, New York, 1931), p. 246. Two drawings of the structure are also to be found in this reference, p. 247.

We have investigated this crystal by the x-ray diffraction method in order to determine the interatomic distances accurately. The N—N distance is of interest in connection with the as yet unsettled question of the effect of formal charge on interatomic distance. The N—H···Cl distance affords further information on hydrogen bonding between nitrogen and chlorine. The structure also provides interesting comparisons with those of hydrazinium difluoride<sup>3</sup> and methylammonium chloride.<sup>4</sup>

### EXPERIMENTAL

Eastman White Label hydrazinium dichloride was dissolved in dilute hydrochloric acid. Slow evaporation of the solution yielded tiny octahedra suitable for x-ray examination. Crystals not over 0.2 mm in greatest dimension were

<sup>3</sup> W. L. Kronberg and D. Harker, *J. Chem. Phys.* 10, 309 (1942).

<sup>4</sup> E. W. Hughes and W. N. Lipscomb, *J. Am. Chem. Soc.* 68, 1970 (1946).

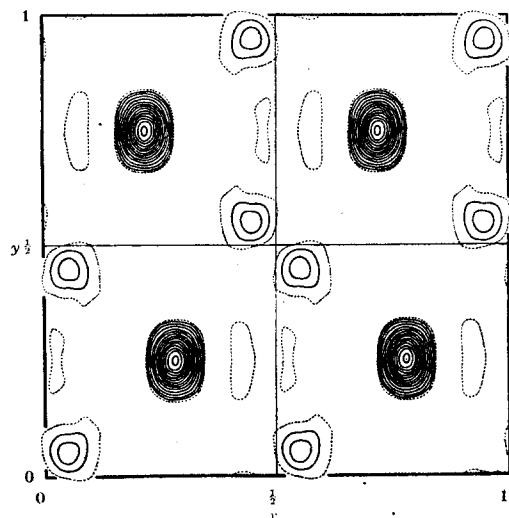


FIG. 1. Fourier projection on (001).

mounted on the x-ray goniometer heads in the usual way. Laue photographs showed that the symmetry class of the crystals was either  $T$  or  $T_h$ . Oscillation photographs were taken with  $\text{CuK}\alpha$  radiation ( $\lambda=1.542\text{\AA}$ ) over the range required to give complete data for the zero, first, and second layer lines. In order to facilitate the visual estimation of intensities the multiple film technique was used.<sup>5</sup> The effect of absorption was ignored, since the size and shape of the crystals were favorable for doing so.

Measurement of the equatorial reflections on the oscillation photographs gave the value  $a_0=7.87\pm0.01\text{\AA}$ , in satisfactory agreement with Wyckoff's value of  $7.89\text{\AA}$ . A very heavily exposed oscillation photograph showed no intermediate layer lines which would require the choice of a larger unit cell. The regular vanishing of ( $hk0$ ) when  $h=2n$ , observed on the oscillation photographs, confirms Wyckoff's choice of the space group  $T_h^6-Pa3$ . The observed density,<sup>6</sup>  $1.4226$ , requires four (calculated  $3.98$ ) molecules of  $\text{N}_2\text{H}_6\text{Cl}_2$  per unit cell. The eight nitrogen atoms lie in the positions<sup>7</sup>  $\pm(uuu)$ ,  $(\frac{1}{2}+u, \frac{1}{2}-u, \bar{u})$ ,  $(\bar{u}, \frac{1}{2}+u, \frac{1}{2}-u)$ ,  $(\frac{1}{2}-u, \bar{u}, \frac{1}{2}+u)$ ; and the eight

chlorine atoms in a set of similar positions  $\pm(vvv)$ , etc.

For the calculation of  $F$  values, the atomic scattering factors of James and Brindley<sup>8</sup> were used. The  $f$  values for  $N$  were increased by  $2f$  of  $H$  as an approximation to include the effect of the hydrogen atoms. All atomic  $f$  values were multiplied by the temperature factor  $\exp -\beta(\sin\theta/\lambda)^2$ , and the value  $\beta=1.5$  was found to give satisfactory agreement between observed and calculated structure factors.

#### DETERMINATION OF THE PARAMETERS

The approximate parameter values of Wyckoff,  $u=0.04$ ,  $v=0.27$ , enable the assignment of signs to the  $F$  values of all of the observed ( $hk0$ ) reflections. A Fourier projection on (001) made with the twenty-three available ( $hk0$ ) reflections is shown in Fig. 1. The smaller resolved peaks represent the nitrogen atoms; the larger peaks represent pairs of chlorine atoms which are too close together in this projection to be resolved. The symmetry of the cell, however, allows an accurate estimation of the chlorine parameter as well as the nitrogen parameter. The values  $u=0.052$  and  $v=0.278$  are indicated by this projection. It may be pointed out that the heights of the two kinds of peaks are in the ratio  $3.9:1$ , whereas the ratio expected,  $2\text{Cl}^-:\text{NH}_3^+$ , is  $36:9=4:1$ . The two small peaks and the asymmetry of the nitrogen peak (dotted in Fig. 1) undoubtedly arise from the omission of reflections which lie outside the limit of copper  $K\alpha$  radiation.

TABLE I. Values of  $F_{hk0}$ .

( $hk0$ )	$F_{\text{obs}}$	$F_{\text{calc}}$	( $hk0$ )	$F_{\text{obs}}$	$F_{\text{calc}}$
200	4.1	-7.8	630	5.5	-5.9
210	3.4	+3.5	640	2.4	-2.1
220	7.3	+13.4	270	1.0	-1.2
230	4.9	-5.2	650	1.3	+1.3
400	5.9	+7.9	800	<0.4	-0.7
410	5.5	-6.9	810	4.8	-4.9
420	5.4	-5.3	470	<0.4	-0.1
430	2.8	+2.1	820	1.1	-1.5
250	<0.4	0.0	660	1.2	+1.1
440	4.3	+4.1	830	3.3	+3.2
600	3.8	-3.8	840	<0.4	0.0
610	4.9	+5.1	670	1.7	-1.8
620	2.3	+2.1	850	3.1	-2.9
450	4.7	-4.3			

<sup>5</sup> J. J. deLange, J. M. Robertson, and I. Woodward, Proc. Roy. Soc. (London) A171, 398 (1939).

<sup>6</sup> H. Schiff and U. Monsacchi, Zeits. f. physik. Chemie 21, 292 (1896).

<sup>7</sup> Internationale Tabellen zur Bestimmung von Kristallstrukturen (Gebrueder Borntraeger, Berlin, 1935), Vol. I, p. 320.

<sup>8</sup> Internationale Tabellen zur Bestimmung von Kristallstrukturen (Gebrueder Borntraeger, Berlin, 1935), Vol. II, p. 571.

Since both nitrogen atoms and chlorine atoms lie on a body diagonal of the unit cube, this crystal is well suited to the application of the Fourier method of calculating the electron density along a line. The general expression for the electron density as a function of the coordinates  $x$ ,  $y$ , and  $z$  simplifies for the case  $x=y=z=d$  to

$$\rho(d) = K \sum_H A_H \cos 2\pi H d,$$

where

$$A_H = \sum_{h+k+l=H} F_{hkl}.$$

In making this summation, all available  $(hkl)$ ,  $(hk1)$ , and  $(hk2)$  data were used, the signs of all  $F$  values being determined from the parameters obtained with the projection on  $(001)$ . The use of equalities of the type  $F_{hkl} = -F_{\bar{h}\bar{k}\bar{l}}$  for  $h=2n$  or  $k=2n$ , etc., increased the number of known  $F$  values to nearly 300. The reflections were classified according to  $h+k+l$ , and the series was summed over  $h+k+l=0$  to 15 from  $d=0$  to  $d=\frac{1}{2}$  in intervals of 0.004 in  $d$ . Both this summation and the projection on  $(001)$  were made with the use of punched cards and International Business Machines.<sup>9</sup> The density function  $\rho(d)$ , the curve labelled OBS in Fig. 2, gives the values  $u=0.052$  and  $v=0.279$ , which are in excellent agreement with the values given by the  $(001)$  projection.

TABLE II. Value of  $F_{hkl}$ .

$(hkl)$	$F_{\text{obs}}$	$F_{\text{calc}}$	$(hkl)$	$F_{\text{obs}}$	$F_{\text{calc}}$	$(hkl)$	$F_{\text{obs}}$	$F_{\text{calc}}$
111	4.3	+6.0	261	5.3	-5.4	812	3.9	+3.9
211	2.4	-1.8	541	1.3	-1.4	182	0.4	+0.4
221	4.3	-4.5	451	3.5	+3.2	742	<0.4	+0.6
311	2.1	+2.6	622	2.8	-3.0	472	1.3	-1.5
222	5.1	-6.3	542	0.6	+0.6	822	<0.4	-0.3
321	1.4	-1.3	452	0.7	+0.9	661	1.6	-1.7
231	1.5	+1.3	631	2.5	+2.3	831	2.5	-2.3
322	1.2	+1.1	361	<0.4	-0.5	381	1.0	-1.1
411	<0.4	0.0	632	3.1	+2.9	751	0.6	+0.7
331	0.4	+0.7	362	1.1	+1.1	662	0.7	-0.7
412	4.4	+4.4	711	0.6	-0.8	832	3.9	-3.7
142	2.0	+2.0	551	0.7	-0.6	382	<0.4	+0.4
332	2.6	-2.1	641	2.0	+1.8	752	1.4	+1.4
422	5.1	+5.8	461	3.7	+3.4	572	<0.4	+0.3
431	3.0	-3.1	721	0.6	-0.6	841	<0.4	0.0
341	3.2	-2.9	271	2.0	+2.0	481	3.1	-3.1
511	0.6	-0.3	552	0.7	-0.8	911	1.0	-1.2
432	4.6	-5.6	642	1.7	+1.6	842	0.5	-0.5
342	2.6	-2.0	722	<0.4	0.0	921	<0.4	-0.1
512	2.4	-2.0	731	1.0	-1.0	291	1.2	-1.2
152	1.5	-1.8	651	3.8	-3.4	761	0.4	-0.5
441	3.9	-3.5	561	1.8	-1.7	671	3.6	+3.4
552	2.5	-2.5	732	1.3	-0.9	762	0.4	-0.4
531	0.6	+0.4	372	0.6	-0.6	672	<0.4	+0.3
442	3.4	-3.4	652	3.4	-3.4	922	<0.4	0.0
532	1.5	+1.7	562	<0.4	-0.2	851	3.3	+2.9
352	<0.4	0.0	811	0.6	+0.6	581	<0.4	-0.1
611	1.7	-1.6	741	1.0	-1.1			
621	0.8	-0.8	471	2.5	-2.6			

<sup>9</sup> P. A. Shaffer, Jr., Verner Schomaker, and Linus Pauling, *J. Chem. Phys.* **14**, 648 (1946).

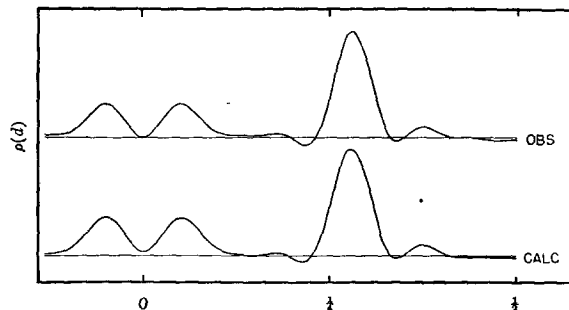


FIG. 2. Electron density along the line  $x=y=z=d$ .

Since data obtained only from the zero, first, and second layer lines were used, no reflections for which  $h$ ,  $k$ , and  $l$  were each  $>3$  were included in the calculation of the function  $\rho(d)$ . Although this function apparently was satisfactorily convergent, the effect of the missing spectra on the positions of the maxima was not known. For this reason, we calculated a second density function, using, in place of the observed  $F$  values, a set of  $F$  values calculated for a structure in which  $u=0.052$  and  $v=0.278$ . The same terms were omitted in the calculation of this second density function as were omitted in the calculation of the first. The resulting curve, labelled CALC in Fig. 2, shows maxima at  $u=0.052$  and  $v=0.278$ . The omission of terms of high order in  $h$ ,  $k$ , and  $l$  did not lead to parameters which were significantly different from those which were assumed, and we may, therefore, infer that the parameters obtained with the observed data are a correspondingly accurate representation of the atomic positions in the crystal.

Since there have been cases in which the inclusion of the scattering of the hydrogen atoms led to a significant improvement in the agreement between observed and calculated values of  $F_{hkl}$ ,<sup>10</sup> we recalculated all  $F_{hkl}$  with  $\sin\theta/\lambda < 0.30$ , placing the twenty-four hydrogen atoms in the general positions<sup>9</sup> of  $Pa3$  with  $x=0.108$ ,  $y=0.039$ , and  $z=0.126$ . These values place groups of three hydrogen atoms 1.03Å from each nitrogen atom, on lines between the nitrogen atom and its closest chlorine neighbors. The over-all effect was a very small improvement of doubtful significance.

<sup>10</sup> For example, H. A. Levy and R. B. Corey, *J. Am. Chem. Soc.* **63**, 2095 (1941). Cf. also reference 6.

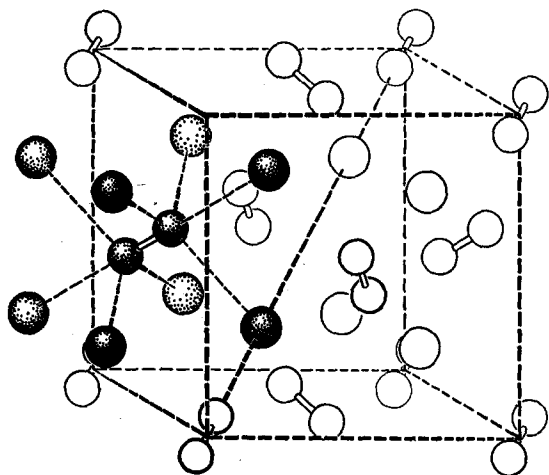


FIG. 3. One unit cell of the crystal, showing the environment of one  $\text{N}_2\text{H}_6^{++}$  group, and the body diagonal along which  $\rho(d)$  was determined. The large balls represent chloride ions, the small balls, nitrogen atoms.

The above results lead us to the parameter values  $u=0.052$  and  $v=0.279$ . We believe it very unlikely that either of these parameters is in error by more than  $\pm 0.0015$ .

The agreement between observed and calculated values of  $F$  is shown in Tables I and II. It is probable that the very strongest reflections, viz., (200), (220), (400), (410), (111), and (222), which are all observed to be too weak, are subject to extinction.

### DISCUSSION

The values of the parameters lead to the following interatomic distances: the N—N distance within the hydrazinium group is 1.42Å, and from the limits of error given for this parameter it is very unlikely that this distance can be in error by more than  $\pm 0.04\text{Å}$ . A drawing of the structure showing the environment of one  $\text{N}_2\text{H}_6^{++}$  group is shown in Fig. 3. Each nitrogen atom has four closest chloride neighbors, one (type I) lies at  $3.10\text{Å} \pm 0.04\text{Å}$  on an extension of the line through the two nitrogen atoms, the other three (type II), also at  $3.10 \pm 0.02\text{Å}$ , form a triangular pyramid with the nitrogen atom, the angles N—N...Cl being  $100^\circ \pm 2^\circ$ . Each chloride ion has four nitrogen neighbors, one of type I and three of type II, and in addition six chloride neighbors which form the equilateral triangle are connected to the nitrogen atom by

hydrogen bonds; the configuration of the  $\text{N}_2\text{H}_6^{++}$  is staggered or *trans*.

It is of interest to compare in detail the structure of  $\text{N}_2\text{H}_6\text{Cl}_2$  with that of  $\text{N}_2\text{H}_6\text{F}_2$ .<sup>3</sup> In both crystals the halide ions form hydrogen bonds leading to N—H...X distances which are shorter than the sums of the respective ionic radii,<sup>11</sup> 0.11Å shorter in the chloride and 0.14Å shorter in the fluoride. In both crystals a nitrogen atom has four closest halide neighbors, three of which are hydrogen bonded, and one of which lies on the extension of the N—N axis. In  $\text{N}_2\text{H}_6\text{Cl}_2$ , this fourth chloride ion lies the same distance from the nitrogen atom as do the other three chloride ions, whereas in  $\text{N}_2\text{H}_6\text{F}_2$  the fourth fluoride ion lies at a distance 0.18Å greater than do the other three. This N...F distance is approximately the sum of the ionic radii. The angle N—N...X is  $100^\circ$  in  $\text{N}_2\text{H}_6\text{Cl}_2$  and  $110^\circ$  in  $\text{N}_2\text{H}_6\text{F}_2$ . The smaller angle and the equality of the four N—H...X distances in the chloride suggest that the fourth chloride ion is subject to significant attraction by the three hydrogen atoms, a situation not unlikely if the actual value of the angle N—N—H is closer to the tetrahedral value  $109^\circ 28'$ . In both crystals a halide ion has four nitrogen neighbors. In  $\text{N}_2\text{H}_6\text{F}_2$ , a fluoride ion has, in addition, three closest fluoride neighbors, at distances 0.68Å greater than the sum of the ionic radii, so that the structure essentially does not depend on any F...F contacts. In  $\text{N}_2\text{H}_6\text{Cl}_2$ , on the other hand, a chloride ion has six closest chloride neighbors, at distances only 0.36Å greater than the radius sum. It is possible that Cl...Cl contacts are of some importance in determining this structure. The major difference between the two structures then arises from the greater coordinating ability of chloride ion as compared to that of fluoride ion. The configuration of the  $\text{N}_2\text{H}_6^{++}$  ion is *trans* in both crystals.

The N—H...Cl distance of 3.10Å may be compared with the N—H...Cl distance of 3.18Å found in  $\text{NH}_3\text{CH}_3\text{Cl}$ .<sup>4</sup> In the latter crystal, the  $\text{CH}_3\text{—NH}_3$  groups are probably rotating, and furthermore only three hydrogen bonds are

<sup>11</sup> An ionic radius of one  $\text{—NH}_3^+$  group of the hydrazinium ion may be taken equal to the ionic radius of 1.54Å for  $\text{NH}_4^+$ , observed in  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$ . This value leads to an ionic radius of 1.41Å when corrected to coordination number 4.

formed, on the average, between a nitrogen atom and four chloride ions. These differences lead to much weaker and consequently longer  $\text{N}-\text{H}\cdots\text{Cl}$  bonds in methylammonium chloride.

The  $\text{N}-\text{N}$  distance in both hydrazinium dichloride and hydrazinium difluoride is the same, 1.42Å. This distance is 0.05Å shorter than the  $\text{N}-\text{N}$  distance in gaseous hydrazine.<sup>12</sup> This shortening has been attributed to the formal charges on the nitrogen atoms.<sup>3</sup> However, since the structure of the  $\text{N}_2\text{H}_6^{++}$  ion for which there are adjacent charges on each nitrogen atom contributes but 25 percent to the normal state of the ion,<sup>3</sup> it seems essentially illogical to attribute a shortening of this magnitude to the formal charges. The formal charge effect, as originally conceived,<sup>13,14</sup> was intended to correct the covalent radius of an atom which had a formal charge of +1 by about  $-0.03\text{Å}$ . Some molecules in which this effect might be expected, together with the available experimental data, are presented in Table III. Because of the uncertainty involved in predicting distances which are involved in single-bond double-bond resonance, only single covalent bonds are included in the

TABLE III.

Bond	Compound	Observed distance	Predicted distance*
$\text{O}-\text{N}^+$	$\text{HNO}_3$	$1.41 \pm 0.02\text{Å}^a$	1.43Å
$\text{C}-\text{N}^+$	$\text{C}(\text{NO}_2)_4$	$1.47 \pm 0.02\text{Å}^b$	1.46Å
	$\text{CH}_3\text{NH}_3\text{Cl}$	$1.46 \pm 0.01\text{Å}^c$	
	$(\text{CH}_3)_3\text{NO}$	$1.49 \pm 0.02\text{Å}^d$	
$\text{N}^+-\text{N}^+$	$\text{N}_2\text{H}_6\text{F}_2$	$1.42 \pm 0.02\text{Å}^e$	1.47Å
	$\text{N}_2\text{H}_6\text{Cl}_2$	$1.42 \pm 0.04\text{Å}^f$	
$\text{C}-\text{S}^+$	$(\text{CH}_3)_2\text{SO}$	$1.84 \pm 0.02\text{Å}^d$	1.81Å
$\text{C}-\text{S}^{++}$	$(\text{CH}_3)_2\text{SO}_2$	$1.81 \pm 0.02\text{Å}^d$	1.81Å

\* Reference 15 in text.

<sup>a</sup> L. R. Maxwell and V. M. Mosley, *Phys. Rev.* **57**, 1079A (1940).

<sup>b</sup> A. J. Stosick, *J. Am. Chem. Soc.* **61**, 1127 (1939).

<sup>c</sup> Reference 4 in text.

<sup>d</sup> R. E. Rundle, Dissertation, California Institute of Technology (1941).

<sup>e</sup> Reference 3 in text.

<sup>f</sup> This determination.

table. The predicted distances are those in the table of revised covalent radii of Schomaker and Stevenson.<sup>15</sup>

It is apparent that the correction for formal charge is not generally applicable. There do not seem to be sufficient experimental data concerning this point so that a satisfactory revision of the original correction can be made. X-ray investigations of a hydroxylammonium salt such as  $\text{NH}_3\text{OHCl}$  and of a metallic peroxide would provide additional information of interest.

<sup>15</sup> V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

<sup>12</sup> P. A. Giguère and V. Schomaker, *J. Am. Chem. Soc.* **65**, 2025 (1943).

<sup>13</sup> N. Elliott, *J. Am. Chem. Soc.* **59**, 1380 (1937).

<sup>14</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 171.