Acta Cryst. (1973). B**29**, 50

The Crystal and Molecular Structure of 2-(*N*-Nitrosomethylamino)acetamide*

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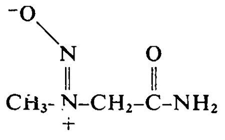
(*Received* 21 *July* 1972; *accepted* 19 *September* 1972)

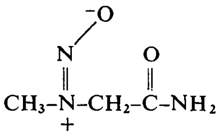
Crystals of 2-(*N*-nitrosomethylamino)acetamide are monoclinic, space group $P2_1/n$, with $a=16{\cdot}681$ (30), $b=4{\cdot}774$ (5), $c=14{\cdot}318$ (15) Å and $\beta=92{\cdot}95(20)°$. Each unit cell contains four molecules of the E isomer and four of the Z isomer. The structural model was refined to $R=0{\cdot}044$ for 1184 independent reflections measured using an automatic diffractometer. Hydrogen bonds from amide groups to carbonyl or nitroso oxygen atoms connect the molecules in sheets parallel to (100).

Kenyon & Rowley (1971) found 2-(*N*-nitrosomethylamino)acetamide as the hydrolysis product of a secondary *N*-nitrosoamine. It crystallized as a mixture of needles and plates. On the basis of n.m.r. spectra they concluded that the needles contained a mixture of the *E* and *Z* isomers:†



$$\mathrm{CH_3{-}\underset{+}{\overset{\overset{^{-}O\diagdown}{N}}{\overset{\|}{N}}}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2}$$

E



$$\mathrm{CH_3{-}\underset{+}{\overset{\overset{\diagup O^{-}}{N}}{\overset{\|}{N}}}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2}$$

Z

In this paper we report a crystal structure determination which confirms this result. We found a 50:50 mixture of the isomers with conformations as shown in Fig. 1.

Experimental

Colorless, needle-like crystals, synthesized by the reaction of sarcosinamide with nitrous acid (Kenyon & Rowley, 1971), were provided by Professor Kenyon of the University of California, Berkeley. A crystal of dimensions 0·066 × 0·042 × 0·111 mm was glued to the tip of a glass fiber in air with the *b* axis parallel to the axis of the fiber. Preliminary X-ray diffraction data were obtained from oscillation and Weissenberg photographs taken with copper radiation. Accurate unit-cell dimensions were determined from measurement of *h*00, 0*k*0, 00*l* reflections using a Picker automatic diffractometer equipped with a full-circle goniostat, graphite monochromator, pulse-height analyzer and PDP-8I computer. Intensity data were collected with the same instrument. The integrated intensity of each reflection was measured using a θ–2θ scan technique with a scanning rate of 1° per min from 1° below the 2θ angle at which $K\alpha_1$ was diffracted to 1° above the 2θ angle at which $K\alpha_2$ was diffracted. Two 10-sec background counts were taken, with the apparatus stationary, 0·5° below and 0·5° above the 2θ angle at which the scanning was begun and ended. Three strong reflections (600, 004, 020) were checked every 100 reflections for crystal decomposition and/or instrument malfunction. The crystal had to be slightly realigned several times during the data collection, which lasted nine days. From the above three 'standard' reflections it was found that there was a 30% decay in the intensities during the experiment. Scale factors were adjusted on the assumption that all reflections decreased at the same rate.

Recorded counts were treated as follows: (recorded counts) × 10 + 4·5 = actual counts. When the background was recorded as zero, it was set equal to 6 (because we do not have a counter for the last digit). The actual counts were converted into structure factors and standard deviations $\sigma(F)$ using the formula given by St. Clair, Zalkin & Templeton (1971), except that the additional term in $\sigma^2(I)$ was $(0{\cdot}06I)^2$.

The absorption coefficient for this compound is $\mu=$

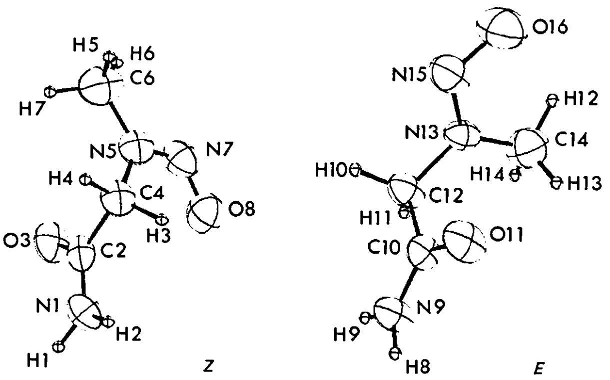


Fig. 1. Perspective drawing of the *E* and *Z* isomers. Thermal boundaries are at the 50% probability level. For this drawing the hydrogen atoms were given artificial thermal parameters of $B=0{\cdot}5$.

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Designated as *entgegen* and *zusammen* (IUPAC, 1970).

9·9 cm^{-1}. No correction for absorption was made; it is estimated that it would affect the intensities by no more than 7%.

Measurements were made of 2444 reflections not excluded by the space group in the hemisphere $\pm h$, k, $\pm l$. Of these, 168 were recorded as less than the background and 408 others were less than one standard deviation above background. When a reflection was measured more than once, the intensities were averaged and its standard deviation was treated as set forth by St. Clair, Zalkin & Templeton (1971). These 2444 reflections represent 1417 unique reflections of which 1184 are greater than one standard deviation.

The two figures were prepared using the program of Johnson (1965).

The ratios of observed and calculated structure factors for the strongest reflections range from 0·95 to 1·05 and give no indication of any significant extinction effect.

Crystal data

The crystals are monoclinic with unit-cell dimensions measured at room temperature (~24°C): $a=16{\cdot}681\pm0{\cdot}030$, $b=4{\cdot}774\pm0{\cdot}005$, $c=14{\cdot}318\pm0{\cdot}015$ Å, $\beta=$

Table 1. *Observed structure factors, standard deviations and differences* (×8·0)

SG=e.s.d. of FOB. DEL=|FOB|−|FCA|. An asterisk indicates zero-weighted data.

92·95 ± 0·2°. There are eight molecules of $C_3H_7N_3O_2$ (four of each isomer) in the unit cell. The calculated density $\varrho = 1{\cdot}367$ g cm^{-3} agrees well with the observed density $\varrho = 1{\cdot}36 \pm 0{\cdot}02$ g cm^{-3} measured by flotation in solutions of chloroform and hexane.

The extinction rules ($h0l$ absent if $h+l=2n+1$ and $0k0$ absent if $k=2n+1$) are characteristic of space group $P2_1/n$. All atoms are in general positions.

Determination of the structure

The structure was solved from statistics. The phases of normalized structure factors E were calculated with the program of Long (1965) which uses Sayre's equation. The 16 possible combinations of signs of four reflections (in addition to three origin determining reflections) were used to calculate probable phases for the 165 reflections whose $|E|$ values were $\geq 1{\cdot}50$. One combination of signs was better than the rest. This solution had a consistency index of 0·80 compared with the next best value of 0·77, and also took the fewest cycles (six) to determine all the signs. The Fourier synthesis of this best E set showed both the E and Z isomers and yielded the coordinates of the 16 nonhydrogen atoms (carbon, nitrogen and oxygen) in the asymmetric unit.

With anisotropic thermal parameters (for the 16 atoms) the full matrix least-squares refinement reduced $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ to 0·089 for 1184 non-zero reflections. The scattering factors of Cromer & Waber (1965) were used for all atoms except hydrogen whose scattering factors are those of Stewart, Davidson & Simpson (1965). All 14 hydrogens except for one in the methyl group of the E isomer showed well defined peaks in a ΔF Fourier synthesis. When, in addition to the 16 nonhydrogen atoms with anisotropic temperature factors, three positional parameters and an isotropic thermal temperature factor were included for each of the 14 hydrogens, refinement gave $R_1 = 0{\cdot}0477$ after four cycles. Further refinements were made with a variation of our least-squares program (written by Arthur Olson)* which uses the scattering factors of Stewart *et al.* (1965) for polarized H atoms. The R value hardly changed ($R_1 = 0{\cdot}0476$), but the hydrogen distances lengthened by about 0·1 Å. Final refinement, using for C, N, and O the scattering factors of Doyle & Turner (1968) and the anomalous dispersion corrections of Cromer & Liberman (1970) reduced R_1 to 0·044 and $R_2 = [\sum w(\Delta F)^2 / \sum w(F_o)^2]^{1/2}$ to 0·052. No parameter shifted more than 2·7% of its estimated standard deviation in the final refinement. The standard deviation of an observation of unit weight was 1·19. Observed structure factors, standard deviations, and values of ΔF are listed in Table 1.

Results and discussion

Final values for atomic coordinates and thermal parameters are given in Tables 2, 3 and 4. Bond distan-

Table 2. *Coordinates of nonhydrogen atoms*

	x	y	z
N(1)	0·2044 (2)	0·6926 (6)	0·3999 (2)
C(2)	0·2823 (2)	0·6506 (5)	0·4120 (2)
O(3)	0·3267 (1)	0·7901 (4)	0·4652 (1)
C(4)	0·3160 (2)	0·4141 (6)	0·3557 (2)
N(5)	0·3997 (1)	0·4585 (5)	0·3391 (2)
C(6)	0·4625 (3)	0·306 (1)	0·3905 (3)
N(7)	0·4219 (2)	0·6529 (6)	0·2816 (2)
O(8)	0·3648 (1)	0·7866 (5)	0·2456 (1)
N(9)	0·8394 (2)	0·4168 (6)	0·1479 (2)
C(10)	0·8483 (1)	0·5837 (5)	0·2205 (2)
O(11)	0·8485 (1)	0·8405 (4)	0·2149 (1)
C(12)	0·8573 (2)	0·4421 (6)	0·3154 (2)
N(13)	0·9008 (1)	0·6173 (5)	0·3823 (1)
C(14)	0·9856 (2)	0·665 (1)	0·3783 (3)
N(15)	0·8540 (2)	0·7544 (6)	0·4391 (2)
O(16)	0·8910 (1)	0·9194 (5)	0·4903 (1)

Table 3. *Anisotropic thermal parameters*

The temperature factor is exp $(-\sum_i \sum_j B_{ij} h_i h_j b_i b_j / 4)$, where b_i is the length of the ith reciprocal cell dimension.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	5·3 (2)	4·1 (1)	4·5 (1)	0·1 (1)	1·0 (1)	−0·9 (1)
C(2)	5·5 (2)	2·2 (1)	2·7 (1)	−0·2 (1)	0·6 (1)	0·1 (1)
O(3)	6·8 (1)	3·9 (1)	3·99 (9)	−0·48 (9)	0·12 (8)	−1·26 (8)
C(4)	5·2 (2)	2·5 (1)	4·1 (1)	−0·2 (1)	0·3 (1)	−0·3 (1)
N(5)	5·0 (1)	2·7 (1)	4·3 (1)	−0·11 (9)	0·53 (9)	−0·4 (1)
C(6)	5·7 (2)	5·4 (2)	7·1 (2)	0·5 (2)	−1·0 (2)	−0·9 (2)
N(7)	5·8 (1)	4·2 (1)	5·3 (1)	0·1 (1)	1·1 (1)	−0·7 (1)
O(8)	7·1 (1)	5·4 (1)	5·3 (1)	0·4 (1)	0·8 (1)	0·9 (1)
N(9)	6·8 (1)	2·1 (1)	3·3 (1)	−0·2 (1)	−0·7 (1)	0·2 (1)
C(10)	4·0 (1)	2·1 (1)	3·5 (1)	0·02 (9)	−0·33 (9)	0·3 (1)
O(11)	7·5 (1)	1·87 (9)	4·4 (1)	0·07 (8)	−0·58 (8)	0·31 (7)
C(12)	5·8 (2)	2·5 (1)	3·4 (1)	−0·4 (1)	−0·6 (1)	0·0 (1)
N(13)	4·5 (1)	2·5 (1)	2·90 (9)	0·39 (8)	0·34 (8)	−0·61 (8)
C(14)	4·0 (2)	7·7 (3)	4·5 (2)	0·1 (2)	0·0 (1)	−0·5 (2)
N(15)	6·7 (1)	4·1 (1)	3·6 (1)	−0·6 (1)	−0·5 (1)	−0·1 (1)
O(16)	7·2 (1)	6·6 (1)	5·7 (1)	0·4 (1)	0·3 (1)	−2·1 (1)

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* This unpublished program uses a complex form factor to represent a noncentric distribution of electron density in the hydrogen atom, with the proton taken as the point of reference. The coordinates which result are therefore an estimate of the proton position, rather than the estimate of some kind of average position of the electron cloud which is given by the traditional X-ray method.

ces and angles are listed in Tables 5 and 6. Corresponding bond distances in the two isomers (Fig. 1) are equal within the experimental accuracy except perhaps the N–N and N–O distances; the latter differ respectively by three and two times the sums of their standard deviations.

Table 4. *Parameters of hydrogen atoms*

	x	*y*	*z*	*B*
H(1)	0·180 (2)	0·825 (8)	0·439 (2)	6·5 (10)
H(2)	0·171 (2)	0·583 (8)	0·361 (2)	5·1 (9)
H(3)	0·280 (2)	0·395 (7)	0·291 (2)	5·1 (7)
H(4)	0·312 (1)	0·253 (6)	0·395 (2)	3·2 (6)
H(5)	0·459 (2)	0·10 (1)	0·370 (3)	9·2 (12)
H(6)	0·516 (2)	0·381 (8)	0·375 (2)	6·0 (10)
H(7)	0·459 (2)	0·326 (9)	0·462 (3)	8·3 (11)
H(8)	0·826 (2)	0·485 (7)	0·089 (2)	4·8 (8)
H(9)	0·839 (2)	0·224 (8)	0·156 (2)	4·6 (8)
H(10)	0·795 (2)	0·397 (8)	0·335 (2)	6·7 (9)
H(11)	0·892 (2)	0·268 (7)	0·307 (2)	4·5 (7)
H(12)	1·010 (2)	0·723 (9)	0·441 (3)	7·9 (10)
H(13)	0·996 (3)	0·79 (2)	0·323 (4)	15·4 (22)
H(14)	1·010 (3)	0·48 (1)	0·362 (4)	11·4 (17)

Table 5. *Bond distances* (Å)

Distances after correction for thermal motion by the riding model are given in parentheses.

Z Molecule		*E* Molecule	
N(1)–C(2)	1·318 (4) (1·335)	N(9)—C(10)	1·312 (4) (1·326)
C(2)–O(3)	1·230 (4) (1·252)	C(10)–O(11)	1·229 (3) (1·252)
C(2)–C(4)	1·513 (4)	C(10)–C(12)	1·518 (4)
C(4)–N(5)	1·444 (4)	C(12)–N(13)	1·439 (4)
N(5)–C(6)	1·445 (5) (1·471)	N(13)–C(14)	1·438 (5) (1·467)
N(5)–N(7)	1·308 (3)	N(13)–N(15)	1·328 (4)
N(7)–O(8)	1·237 (4) (1·250)	N(15)–O(16)	1·223 (3) (1·241)
N(1)–H(1)	0·96 (4)	N(9)—H(8)	0·92 (3)
N(1)–H(2)	0·93 (4)	N(9)—H(9)	0·93 (4)
C(4)–H(3)	1·08 (3)	C(12)–H(10)	1·12 (3)
C(4)–H(4)	0·95 (3)	C(12)–H(11)	1·02 (3)
C(6)–H(5)	1·04 (5)	C(14)–H(12)	1·01 (4)
C(6)–H(6)	1·00 (4)	C(14)–H(13)	1·02 (7)
C(6)–H(7)	1·04 (4)	C(14)–H(14)	0·99 (6)
N(1)···O(16)	2·948 (5)	N(9)···O(3)	2·965 (4)
N(1)···O(8)	3·030 (5)	N(9)···O(11)	2·915 (4)

Table 6. *Bond angles* (°)

Z Molecule		*E* Molecule	
N(1)–C(2)–O(3)	123·9 (3)	N(9)—C(10)–O(11)	123·7 (3)
N(1)–C(2)–C(4)	115·8 (3)	N(9)—C(10)–C(12)	116·2 (3)
O(3)–C(2)–C(4)	120·3 (3)	O(11)–C(10)–C(12)	120·2 (2)
C(2)–C(4)–N(5)	111·6 (3)	C(10)–C(12)–N(13)	111·1 (2)
C(4)–N(5)–C(6)	121·6 (4)	C(12)–N(13)–C(14)	121·9 (3)
C(6)–N(5)–N(7)	117·2 (4)	C(14)–N(13)–N(15)	123·8 (4)
C(4)–N(5)–N(7)	121·1 (3)	C(12)–N(13)–N(15)	113·7 (3)
N(5)–N(7)–O(8)	113·0 (3)	N(13)–N(15)–O(16)	113·0 (2)
C(2)–N(1)–O(16)	125·6 (2)	C(10)–N(9)—O(3)	114·4 (2)
C(2)–N(1)–O(8)	109·3 (2)	C(10)–N(9)—O(11)	108·1 (2)
C(2)–N(1)–H(1)	119 (2)	C(10)–N(9)—H(8)	121 (2)
C(2)–N(1)–H(2)	123 (2)	C(10)–N(9)—H(9)	120 (2)
H(1)–N(1)–H(2)	118 (4)	H(8)—N(9)—H(9)	118 (3)
H(5)–C(6)–H(6)	109 (4)	H(12)–C(14)–H(13)	118 (5)
H(5)–C(6)–H(7)	111 (5)	H(12)–C(14)–H(14)	107 (4)
H(6)–C(6)–H(7)	107 (4)	H(13)–C(14)–H(14)	104 (7)

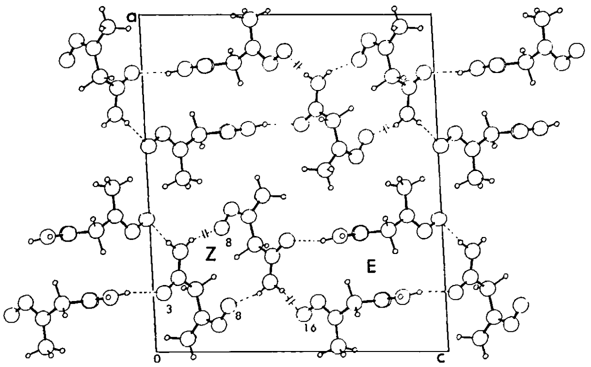

Fig. 2. Projection of the unit cell looking down the *b* axis. Hydrogen atoms are represented by the small circles. The dotted lines are hydrogen bonds. When the line is broken the bond is to the molecule above or below. The numbers identify the different oxygen atoms.

The dimensions of the amide groups (corrected for thermal motion according to the riding model) are in excellent agreement with the corresponding bond lengths C–N = 1·338 (7) and C–O = 1·258 (6) Å reported by Denne & Small (1971) for acetamide, and C–N = 1·334 (4) and C–O = 1·254 (4) Å reported by Chieh, Subramanian and Trotter (1970; in this paper the abstract cites C–O = 1·253 Å, in conflict with the value in the text) for malonamide. Before the correction, the agreement is slightly less for the C–O bonds. For the amide-methylene bond (uncorrected for thermal motion) our values C–C = 1·513 (4), 1·518 (4) Å are close to C–C = 1·507 (4) in malonamide (Chieh, Subramanian & Trotter, 1970). The C–N bond lengths exhibit the partial double-bond character typical of amides. The bond lengths in the vicinity of the nitroso groups agree within 0·03 Å or better with corresponding bonds in gaseous nitrosodimethylamine as determined by Rademacher, Stølevik & Lüttke (1968) by electron diffraction: N–O = 1·235 (2), N–N = 1·344 (2), and N–C = 1·461 (2) Å. We have failed to find reports of accurate determinations in the solid phase of structures of strictly analogous molecules. Boer & Turley (1969) have reviewed the rather discordant results for several nitroso monomers and dimers. In dimethylnitrosamine copper(II) chloride, Klement (1969) found N–O = 1·22 (2), N–N = 1·29 (2), and N–C = 1·46 (3) and 1·47 (3) Å.

Each amide hydrogen atom is pointed towards an oxygen atom at a reasonable distance for an N–H···O hydrogen bond. These bond lengths are listed in Table 5. These bonds, as shown in Fig. 2, connect the amide of the *Z* molecule to nitroso oxygen atoms of each kind of molecule. The amide of the *E* molecule is connected to carbonyl oxygen atoms of each kind of molecule. These bonds connect the molecules in infinite layers parallel to **b** and **c**.

We thank Professor George Kenyon and Dr Gerald Rowley for providing the crystals for this study.

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Acta Cryst. (1973). B**29**, 54

The Structure of a Ring-*D*-Bridged Steroid†

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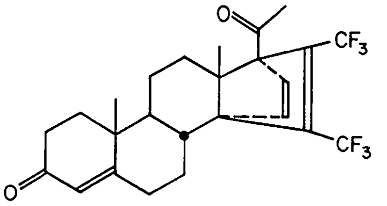
(*Received* 19 *June* 1972; *accepted* 14 *September* 1972)

14α,17α-Etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione, $C_{25}H_{26}O_2F_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z=4$) with cell dimensions $a=20{\cdot}523\pm0{\cdot}003$, $b=14{\cdot}224\pm0{\cdot}003$, $c=7{\cdot}833\pm0{\cdot}003$ Å. Crystal densities are $D_m=1{\cdot}36$ and $D_x=1{\cdot}37$ g cm^{-3}. Intensity data were collected at room temperature with an automatic four-circle diffractometer. The structure was solved by direct methods and refined by the least-squares procedure to a final value of $R=0{\cdot}061$ for 2369 observed reflexions. The conformation of ring *A* is intermediate between a half-chair and a sofa. Rings *B* and *C*, which are *trans* fused, are chair shaped. The geometry of the bicyclic system consisting of rings *D* and *D** is very similar to that of norbornadiene.

Introduction

In the course of their chemical and pharmacological studies of steroids with bridged *D*-rings, Solo and his colleagues observed that, in compounds containing two double bonds in the bicyclic system, the hydrogen atoms attached to C(18) are unusually deshielded, as shown by a shift of 0·30 ppm in the n.m.r. spectrum (Solo, Eng & Singh, 1972). In the hope that the precise knowledge of the geometry of the bicyclic system and its vicinity would yield some explanation of this phenomenon an X-ray analysis of 14α,17α-etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione (I) was undertaken.



Experimental

Crystal data

14α,17α-etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione, $C_{25}H_{26}O_2F_6$; F. W. 472·47; orthorhombic:

$a=20{\cdot}523\pm0{\cdot}003$ Å
$b=14{\cdot}224\pm0{\cdot}003$
$c=\ 7{\cdot}833\pm0{\cdot}003$
$V=2286{\cdot}6$ Å^3
$F(000)=984$.
$Z=4$
$D_x=1{\cdot}37$ g cm^{-3}
$D_m=1{\cdot}36$ (flotation)
$\mu=10{\cdot}5$ cm^{-1} (Cu $K\alpha$)

Absent reflexions: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group: $P2_12_12_1$.

The material was obtained by a Diels–Alder addition of hexafluoro-2-butyne to 3β-acetoxy-20-keto-5,14,16-pregnatriene, followed by a hydrolysis of the acetate group and an oxidation of the resulting alcohol (Solo & Singh, 1967). The product was crystallized from t-butyl propionate to give colourless prisms (elongated parallel to **c**) with a diamond-shaped base. One of the crystals was cut to a size of 0·3 × 0·4 × 0·6 mm and mounted with **c** parallel to φ on a card-controlled Picker four-circle diffractometer equipped with a Cu

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† Issued as N.R.C.C. No. 12903.