Fig. 4. Dessin stéréoscopique montrant la configuration de la molécule et l'agitation thermique des atomes C, N et O (les ellipsoïdes correspondent à une probabilité de 50%). Les atomes d'hydrogène des groupes méthyl ne sont pas représentés.

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ThCN Crystal Structure*

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The crystal structure of ThCN was determined from X-ray and neutron diffraction powder patterns as being C-centered monoclinic, space group $C2/m$ (C_{2h}^3), with the unit-cell dimensions $a_0 = 7.0249 \pm 0.0006$, $b_0 = 3.9461 \pm 0.0002$, $c_0 = 7.2763 \pm 0.0009$ Å, and $\beta = 95.67 \pm 0.01°$. Atomic positions are $(000)(\frac{1}{2}\frac{1}{2}0) +$ 4Th in $\pm (x_{Th}, 0, z_{Th})$, 4C in $\pm (x_C, 0, z_C)$, and 4N in $\pm (x_N, 0, z_N)$, where $x_{Th} = 0.177 \pm 0.005$, $z_{Th} = 0.200 \pm 0.003$, $x_C = 0.444 \pm 0.005$, $z_C = 0.560 \pm 0.005$, $x_N = 0.153 \pm 0.005$, and $z_N = 0.875 \pm 0.005$. The carbon atoms in the structure occur as triply bonded pairs.

Introduction

The ThCN compound was first described in a report of investigation of the Th–C–N phase system (Benz & Troxel, 1971). Earliest preparations of the compound were impure. Difficulty with preparing pure ThCN was traced to a strong coupling of carbon flux with the nitrogen flux, causing a redistribution of carbon during reaction of ThC with nitrogen (Benz, 1971). Eventually, preparations were obtained that showed no impurities detectable in Debye–Scherrer powder patterns of samples. Composition of the compound, based on

chemical analysis of such preparations, was reported as $ThC_{0.96 \pm 0.02}N_{0.96 \pm 0.02}$, in which the uncertainty represents the observed range of reproducibility of independent preparations (Benz & Troxel, 1971).

Experimental

ThCN was prepared in 3-gram quantities by the reaction of powder $ThC_{1.00 \pm 0.01}$ with 1 atmosphere of nitrogen for 1 hour in a tungsten crucible at 1800 to 1850°C. With nitrogen deduced from weight gain, and the assumption of no thorium or carbon loss, the composition of these preparations is calculated as $ThC_{1.00 \pm 0.01}N_{0.99 \pm 0.02}$.

X-ray diffraction powder patterns were made with nickel-filtered copper radiation. Powder diagrams were obtained with both a Debye–Scherrer camera and a

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Table 1. *X-ray diffraction data for powder* ThCN *as obtained with a diffractometer*

(Copper $K\alpha_1$, $\lambda = 1.54051$ Å)

	2θ		Relative intensities	
hkl	Observed	Calculated	Observed	Calculated*
001	12·22°	12·21°	27	26·7
002	24·57	24·57	41	37·5
200	25·46	25·46	26	20·2
110	25·91	25·91	21	20·4
20$\bar{1}$	27·19	27·19	6	11·2
11$\bar{1}$	28·17	28·17	100	100·0
111	29·32	29·28	30	28·5
201	29·44	29·43	37	39·8
20$\bar{2}$	33·81	33·81	22	24·1
11$\bar{2}$	35·09	35·09	0·3	0·4
112	36·90	36·90	39·0	38·0
003	37·23	37·22	18·0	18·8
202	37·47	37·46	0·3	0·6
20$\bar{3}$	–	43·37	nil	0·0
11$\bar{3}$	44·79	44·79	30	27·4
310	45·17	45·15	40	34·3
31$\bar{1}$	45·88	45·85	8	8·3
020	45·95	45·96	20	18·0
113	47·00	47·01	1	1·3
021	47·76	47·73	3	2·3
203	47·82	47·83	11	11·9
311	–	48·03	nil	0·3
31$\bar{2}$	50·02	50·02	11	10·3
004	50·37	50·37	1	0·6
400	52·3	52·30	1	0·9
40$\bar{1}$	52·6	52·60	10	9·5
022	52·78	52·80	14	11·2
220	53·27	53·27	8	6·4
312	54·03	54·06	12	13·4
22$\bar{1}$	54·17	54·22	7	4·0
02$\bar{4}$	54·70	54·70	7	8·0
401	55·23	55·23	5	4·5
221	55·51	55·52	16	15·6
40$\bar{2}$	56·08	56·08	1	1·0
11$\bar{4}$	56·22	56·23	9	8·6
31$\bar{3}$	57·09	57·09	13	12·5
22$\bar{2}$	58·26	58·26	12	11·5
114	58·72	58·74	13	12·1
204	59·73	59·76	2	2·6
023	60·56	60·56	8	10·0
222	60·70	60·72	0·3	0·3
402	61·06	61·06	4	3·8
40$\bar{3}$	62·37	62·39	3	4·8
313	62·60	62·62	8	7·5
005	62·24	64·27	8	5·2
22$\bar{3}$	–	65·03	nil	0·0
31$\bar{4}$	–	66·50	nil	0·0
20$\bar{5}$	67·47	67·46	1	1·1
223	68·49	68·49	8	8·3
11$\bar{5}$	69·08	69·08	2	1·5
403	69·34	69·38	1	0·7
024	70·54	70·54	0·5	0·2
40$\bar{4}$	71·10	71·13	3	2·7
51$\bar{1}$	71·50	{ 71·50	7	{ 1·1
510		71·53		4·5
115	71·91	71·91	0·5	1·0
420	72·17	72·14	0·3	0·7
42$\bar{1}$	72·39	72·39	8	7·3

$$* \ 13\cdot84 \times 10^{-6} j \left[\frac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta}\right] F^2,$$ where j is the multiplicity,

F is the structure factor calculated with the Debye–Waller thermal parameter values of $B_{Th} = 0.2$ and $B_C = B_N = 0.4$, and atomic scattering factors listed in *International Tables for X-ray Crystallography* (1959).

Norelco Geiger counter X-ray diffractomerer. Neutron diffraction powder patterns were made at the Omega West Reactor in the Los Alamos Scientific Laboratory. Powder ThCN was sandwiched in the shape of a slab between two parallel sheets of a 63Ti–37Zr alloy (Sidhu, Heaton, Zauberis & Campos, 1956), and diffracted neutrons with the wave length $\lambda = 1.142$ Å were counted with a 70 cm long BF_3 detector. Partial X-ray and neutron diffraction powder patterns of ThCn are listed in columns 2 and 4 of Tables 1, 2 and 3.

Interpretation

The X-ray diffraction pattern of ThCN could not be interpreted on the basis of orthorhombic or higher symmetry. Accordingly, the possibility of monoclinic symmetry was examined. The method previously described for interpreting the complicated diffraction patterns of monoclinic α- and β-phases of plutonium metal was used with success (Zachariasen, 1963).

Table 2. *High-angle X-ray diffraction powder pattern data for* ThCN *as obtained from a film*

(Copper $K\alpha_1$, $\lambda = 1.54051$Å)

	$10^3 \times \sin^2 \theta$		Relative intensity	
hkl	Observed	Calculated	Observed	Calculated†
62$\bar{6}$	0·9132	0·9135	$W+$	3·9
009	0·9177	{ 0·9166	$W+$	{ 0·9
24$\bar{5}$		0·9179		2·9
82$\bar{1}$	0·9225	0·9222	F	0·6
20$\bar{9}$	0·9230	0·9235	W	5·5
137	0·9255	0·9258	$W+$	10·3
318	0·9270	{ 0·9272	F	{ 4·9
606		0·9278		0·0
820	0·9289	0·9294	$M-$	9·9
73$\bar{1}$		0·9329		11·1
443	0·9332	0·9335	$M+$	2·0
803		0·9344		6·8
82$\bar{2}$		0·9376		10·1
730	0·9373*	0·9378	$M-$	0·4
625		0·9419		9·9
716	0·9415	0·9431	M	13·8
11$\bar{9}$	0·9458*	0·9460	$W-$	7·8
44$\bar{4}$	0·9473	0·9479	W	9·9
73$\bar{2}$	0·9501	0·9506	$W-$	4·5
33$\bar{7}$	0·9580	0·9580	W	5·8
821	0·9600	0·9593	W	6·9
228		0·9623		13·6
245	0·9640	0·9642	diffuse S	7·3
150		0·9647		3·2
731		0·9653		14·8
427	0·9658	0·9660	$W+$	10·1
80$\bar{5}$	0·9695*	0·9673	$W+$	6·1
518	0·9734	{ 0·9732	$M-$	{ 0·9
15$\bar{1}$		0·9737		20·7
82$\bar{3}$	0·9757	0·9757	W	3·1
517	0·9781	{ 0·9772	M	{ 0·4
151		0·9783		8·0
53$\bar{6}$	0·9840	0·9843	$W-$	4·7
535	0·9873	{ 0·9872	S	{ 20·5
119		0·9877		29·4
73$\bar{3}$	0·9911*	0·9910	M	19·3

* Coincident with the α_2 component of the preceding reflection.
† Calculated as described in the footnote of Table 1.

Table 3. *Neutron diffraction data for powder*
ThCN ($\lambda = 1.142$ Å)

	2θ		Relative intensities		
hkl	Observed	Calculated	$\int C \sin^2 \omega^a \, \omega^*$	Calculated†	
001	9·05°	9·05°	39	39	
002	18·1	18·15	38	37	
200	18·8	18·80	54	54	
110	19·1	19·13	77	76	
20$\bar{1}$	20·1	20·07	94	93	
11$\bar{1}$	20·8	20·79	1005	991	
111 ⎱	21·7	⎰ 21·60	829	419 ⎱	821
201 ⎰		⎱ 21·71		402 ⎰	
20$\bar{2}$	—	24·90	3	5	
11$\bar{2}$	25·8	25·83	402	419	
112 ⎱		27·13		293 ⎱	
003 ⎬	27·4	27·37	1810	828 ⎬	1805
202 ⎰		27·54		684 ⎰	
20$\bar{3}$	—	31·79	3	6	
11$\bar{3}$ ⎱		32·81		1820 ⎱	
310 ⎬	33·1	33·07	7590	2740 ⎬	7280
31$\bar{1}$ ⎰		33·57		840 ⎰	
020 ⎰		33·64		1880 ⎰	

* Observed peak intensities, where the range of integration extends over the peak width and C is the number of neutrons counted at the angle $\omega = 2\theta$ degrees.

† $[11\cdot2 \times 10^{24}(\text{cm}^{-2})]$ exp $(-0\cdot2104 \sec \theta)jF_2$, where exp $(-0\cdot2104 \sec \theta)$ is an absorption factor, j is the multiplicity, and F is the structure factor calculated with the Debye–Waller thermal parameter values of $B_{Th} = 0\cdot2$ and $B_C = B_N = 0\cdot4$, and the neutron scattering amplitudes $b_{Th} = 1\cdot01$, $b_C = 0\cdot661$, and $b_N = 0\cdot94$.

Room-temperature unit-cell dimensions, and their reproducibilities as calculated from the high-angle reflections in powder photographs, are $a_o = 7\cdot0249 \pm 0\cdot0006$, $b_o = 3\cdot9461 \pm 0\cdot0002$, $c_o = 7\cdot2763 \pm 0\cdot0009$ Å, and $\beta = 95\cdot67 \pm 0\cdot01°$. The translation lattice is C-centered, since only reflections with $H + K$ even were observed. There are no other systematic extinctions.

The observed volume of the unit cell is compatible only with four formula units of ThCN, corresponding to a density of $8\cdot54^{+0\cdot0\cdot1}_{-0\cdot05}$ g.cm^{-3}. The uncertainty is largely due to uncertainty in composition.

In the X-ray diffraction pattern, carbon and nitrogen atoms have very little effect on the diffraction intensities. Indeed, excellent intensity agreement was obtained by placing four thorium atoms in positions $\pm (x0z) (x+\frac{1}{2},\frac{1}{2},z)$ with $x = 0\cdot18$ and $z = 0\cdot20$. These positions suggest the space group $C2/m$ or $C2$.

Neutron diffraction data were needed to find the positions of the light atoms. The structure finally deduced is:

Space group $C2/m$ (C^3_{2h})
(000) ($\frac{1}{2}\frac{1}{2}0$)+
4Th in $\pm (x_{Th}, 0, z_{Th})$
4C in $\pm (x_C, 0, z_C)$
4N in $\pm (x_N, 0, z_N)$,

where the position-parameter values giving the best agreement of calculated with observed intensity data were found to be $x_{Th} = 0\cdot177 \pm 0\cdot005$, $z_{Th} = 0\cdot200 \pm 0\cdot003$, $x_c = 0\cdot444 \pm 0\cdot005$, $z_c = 0\cdot560 \pm 0\cdot005$, $x_N = 0\cdot153 \pm 0\cdot005$, and $z_N = 0\cdot875 \pm 0\cdot005$. As seen in Tables 1, 2,

and 3, both the X-ray and neutron diffraction relative intensities, calculated on the basis of this structure, are in satisfactory agreement with those observed. Corresponding interatomic distances are listed in Table 4.

Table 4. *Interatomic distances in the* ThCN *lattice*

C–C(1)	$1\cdot23 \pm 0\cdot10$ Å
Th–N(1)	$2\cdot33 \pm 0\cdot09$
Th–N(1)	$2\cdot35 \pm 0\cdot08$
Th–N(2)	$2\cdot40 \pm 0\cdot05$
Th–C(1)	$3\cdot04 \pm 0\cdot10$
Th–C(1)	$3\cdot07 \pm 0\cdot10$
Th–C(2)	$2\cdot82 \pm 0\cdot07$

Discussion

The carbon atoms occur in pairs in the structure. The short carbon–carbon distance of $1\cdot23 \pm 0\cdot10$ Å corresponds to a triple bond. Accordingly, the formula of the compound might be written as $Th_2C \equiv CN_2$.

Since three of the four valence units of carbon are used within the C_2 group, carbon in this compound acts as a univalent atom with respect to thorium. Thus, there is valence balance with the normal valence of three for nitrogen and four for thorium.

Each thorium atom is bonded to four nitrogen atoms and to four carbon atoms. Conversely, each nitrogen atom is bonded to four thorium atoms, and each carbon is bonded to four thorium atoms and to one carbon atom. Since all valences are in balance
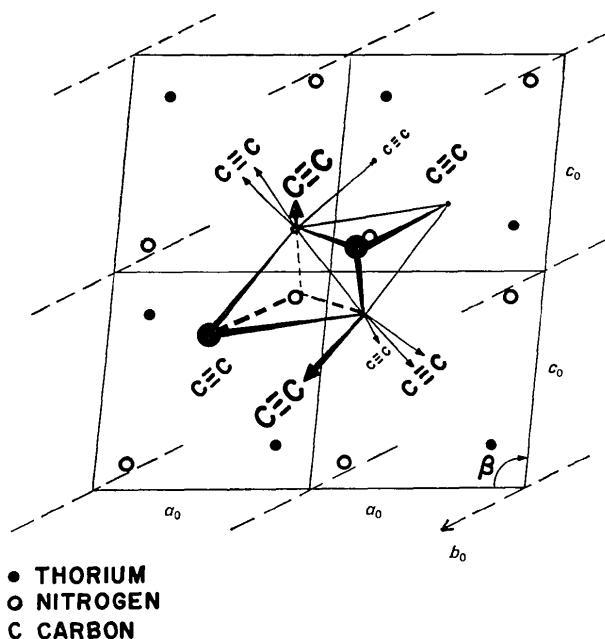

● THORIUM
○ NITROGEN
C CARBON

Fig. 1. Illustration of atoms in the a_0–c_0 plane of four adjacent unit cells, showing the distorted tetrahedral arrangement of thorium about the two central nitrogen atoms. The Th–C distances shown as arrows are shorter for bonds to only one ($2\cdot82$ Å, out of a_0–c_0 plane) than for bonds to both ($3\cdot06$ Å, in a_0–c_0 plane) carbon atoms of a pair.

with the assumed triple bond within the C_2 group, there is no reason to assume the presence of true thorium–thorium bonds.

The four N–Th bonds are directed toward the corners of a slightly distorted tetrahedron, as illustrated in Fig. 1. Within experimental error, the N–Th bonds are of equal length, 2·36 Å. A great many compounds have structures with a nitrogen atom tetrahedrally bonded to four thorium atoms, and averages of the reported values for the N–Th bond lengths in such compounds range from 2·34 to 2·41 Å (Benz & Zachariasen, 1966, 1969, 1970; Bowman & Arnold, 1971).

When a thorium atom is bonded to both carbon atoms of a C_2 pair, the bond length is considerably longer (3·06 Å) than the value of 2·82 Å, corresponding to binding to only one carbon of a pair. The mean Th–C bond length of 2·98 Å is large compared with the Th–N bond length of 2·36 Å. However, it should be remembered that the carbon atom is effectively univalent with respect to thorium in ThCN and that, hence, the strength of a Th–C bond is only 0·25. In the ThC structure, the bond strength is 0·67 and the bond length is 2·67 Å. The ThC_2 structure (Bowman, Krikorian, Arnold, Wallace & Nereson, 1968) also contains C_2 groups, but the carbon–carbon distance of $1·32 \pm 0·04$ Å corresponds to the formula ThC=C and, thus, the carbon is effectively divalent with respect to thorium. In ThC_2, the mean strength of a Th–C bond is 0·40 and the mean bond length is 2·74 Å.

The weakness of the Th–C bonds in the ThCN structure must cause excellent cleavage parallel to (001), and must also be responsible for the low density of the compound. The volume per thorium atom in ThCN is 50·4 Å^3, compared to the values of 46·4 Å^3 for ThC_2 and 43·8 Å^3 for ThO_2.

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The Crystal and Molecular Structure of
12-Methyl-11,13-dioxo-12-aza-pentacyclo[4.4.3.0.^{1,6}0^{2,10}.0^{5,7}]trideca-3,8-diene

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Crystals of the title compound, $C_{13}H_{11}O_2N$, are orthorhombic, space group $Fdd2$, $Z=8$, $a=27·289 \pm 0·004$, $b=13·108 \pm 0·005$, $c=9·165 \pm 0·002$ Å, $D_x=1·362$ g.cm^{-3}. Data for 454 reflections were collected at room temperature on a Picker automated diffractometer. The structure was solved by direct methods, using a computerized multiple-solution procedure, and it was refined by full-matrix least-squares methods to a final R on F of 0·046, with 377 observed reflections. The average e.s.d.'s of the bond lengths and angles not involving hydrogen are about 0·008 Å and 0·5°, respectively. Bond lengths and angles were corrected for thermal motion. Some C–C single bonds are found to be significantly shorter than the normal C–C single bond length of 1·54 Å. The shortening of the C–C bonds is explained by the conjugation of the C=O bond and C=C bond with the three-membered ring.

Introduction

Crystals of what was presumed to be the title compound, $C_{13}H_{11}O_2N$ (III), were obtained from Professor David Ginsburg of the Technion, Haifa, Israel. This compound is the first stable derivative of the long sought, but never isolated, tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-diene (I).