

The Crystal and Molecular Structure of α,α,N -Triphenylnitron

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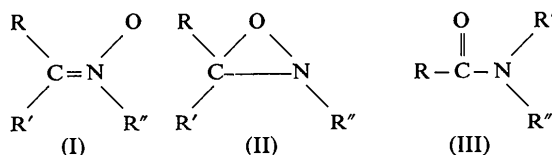
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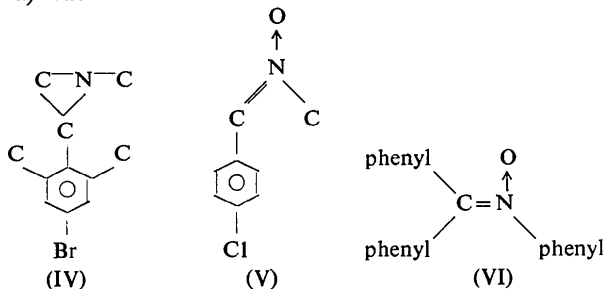
The crystal and molecular structure of triphenylnitron has been determined by a single-crystal X-ray diffraction study using counter data. The compound crystallizes in the orthorhombic space group, *Pbca*, with $a = 17.846$ (2), $b = 8.869$ (1), and $c = 18.192$ (2) Å for $Z = 8$. The structure was solved by the symbolic addition procedure and refined by block-diagonal least-squares calculations to $R = 0.047$ for 1604 statistically significant reflections. The C–N bond length is 1.327 Å, and the N–O bond distance is 1.300 Å.

Introduction

It is now generally accepted that photochemical reactions of most nitrones initially involve the isomerization to the corresponding oxaziridines (Spence, Taylor & Buchardt, 1970). The thermal instability of the oxaziridine towards rearrangement to the corresponding amide first obscured this fact. Indeed stable oxaziridines with aryl substituent are still rare. Thus when α,α,N -triphenylnitron (I) ($R = R' = R'' = \text{phenyl}$) is irradiated, N,N -diphenylbenzamide (III) is isolated (Scheibaum, 1964). Recently however, triphenyloxaziridine (II) has been isolated and shown to be reasonably stable (Ono, 1969).



Most stable oxaziridines have an alkyl substituent on the nitrogen and moreover the only crystal structure of an oxaziridine that has been published to date is the N -alkyl substituted derivative (IV) (Jerslev, 1967). Moreover, the only crystal structure determination of a nitron has also been that of an N -alkyl substituted derivative (V), (Folting, Jerslev & Lipscomb, 1964) although aryl substituted nitrones are stable. In order to aid us in rationalizing why the aryl substituted nitrones undergo rearrangement to the stable amide and not to the oxaziridine, and in view of other interests in the unusual photochemical properties of this compound, the crystal structure of α,α,N -triphenylnitron (VI) was undertaken.



Experimental

Single crystals of α,α,N -triphenylnitron ($\text{C}_{19}\text{H}_{15}\text{NO}$) were kindly provided by Professor G.W. Griffin of L.S.U. in New Orleans. A nicely formed rectangularly shaped crystal ($0.19 \times 0.14 \times 0.28$ mm) was mounted with the $[00l]$ axis coincident with the polar axis, φ , of a General Electric XRD-5 diffractometer. Plots of the reciprocal lattice revealed mmm symmetry with systematic extinctions uniquely identifying the space group as *Pbca*; for $0kl$, $k = 2n + 1$; for $h0l$, $l = 2n + 1$ and for $hk0$, $h = 2n + 1$. Least-squares lattice constants were determined from a fit of 14 measurements of the copper $K\alpha_1$ - $K\alpha_2$ doublet at $2\theta > 67^\circ$ measured under fine conditions (1° take-off angle and 0.05° slit). The

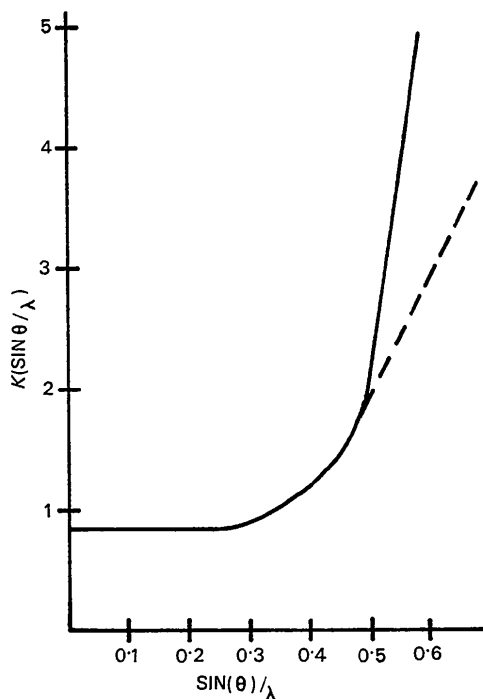


Fig. 1. $K(s)$ -curve. Solid line is that determined from Wilson statistics; dashed line is that ultimately used in the structure determination.

resultant lattice constants and their estimated standard deviations are $a = 17.846 \pm 0.002$, $b = 8.869 \pm 0.001$, $c = 18.192 \pm 0.002$ Å.

The calculated density, 1.259 g. cm^{-3} assuming eight molecules per unit cell, agrees well with the experimental density, 1.26 g. cm^{-3} (by flotation methods).

Three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using Cu $K\alpha$ radiation and balanced nickel and cobalt filters. A total of 2472 unique intensities were measured to a 2θ limit of 120° ($d = 0.889$ Å). Of these, 1604 (65%) were considered statistically significant by the criterion

$$[I_{\text{Ni}} - 2\sigma(I_{\text{Ni}})] - [I_{\text{Co}} + 2\sigma(I_{\text{Co}})] > 100 \text{ counts.}$$

The intensities were corrected for α_1 - α_2 splitting as a function of 2θ (Tulinsky, Worthington & Pignataro, 1964) and for absorption as a function of φ (linear $\mu = 6.20$ cm^{-1} and only a 6% difference in a φ -scan

at $\chi = 90.0^\circ$). Lorentz-polarization corrections were made and the intensities were reduced to structure amplitudes in the usual manner.

Structure determination

Normalized structure magnitudes, $|E|$, were calculated using a K -curve (Karle, Hauptman & Christ, 1958). Because the crystal diffracted only weakly for high-angle reflections, the K -curve showed a sharper increase at higher $\sin \theta/\lambda$ than is normally expected. Numerous attempts were made to solve the structure by the symbolic addition procedure using E 's normalized by the solid K -curve shown in Fig. 1. Finally, the E 's were recalculated using the dashed K -curve in the same Figure. The phases of 249 E 's (including only three-dimensional data) from a total of 324 E 's (including all data) with $|E| > 1.5$ were determined in terms of one symbolic sign by the symbolic addition procedure with no phase being accepted below a probabi-

Table 1. Fractional coordinates and thermal parameters

All values are $\times 10^4$. Estimated standard deviations (in parentheses) refer to the last decimal place. Anisotropic temperature factors of the form:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Hydrogen isotropic temperature factors of the form:

$$\exp\left(-\beta_{11} \frac{\sin^2\theta}{\lambda^2}\right).$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2264 (1)	2631 (3)	2247 (1)	19 (1)	114 (5)	23 (1)	3 (2)	0 (1)	8 (2)
N(2)	2271 (1)	2518 (3)	2945 (1)	17 (1)	153 (4)	29 (1)	1 (2)	-3 (1)	21 (2)
O(3)	2954 (1)	2309 (3)	3171 (1)	20 (1)	317 (5)	42 (1)	14 (2)	-5 (1)	42 (2)
C(4)	2617 (1)	2595 (3)	1653 (1)	21 (1)	123 (5)	26 (1)	6 (2)	1 (1)	11 (2)
C(5)	2408 (2)	2017 (4)	981 (1)	22 (1)	206 (7)	29 (1)	15 (2)	2 (1)	6 (2)
C(6)	2900 (2)	2001 (4)	399 (2)	42 (1)	247 (9)	27 (1)	31 (3)	3 (1)	3 (3)
C(7)	3618 (2)	2562 (4)	473 (2)	39 (1)	195 (7)	43 (1)	18 (3)	18 (1)	24 (3)
C(8)	3829 (2)	3148 (4)	1139 (2)	30 (1)	170 (7)	61 (2)	-7 (3)	16 (1)	9 (3)
C(9)	3343 (2)	3151 (4)	1721 (2)	27 (1)	157 (6)	39 (1)	-18 (2)	6 (1)	0 (2)
C(10)	1259 (1)	2816 (3)	2058 (1)	17 (1)	100 (5)	21 (1)	1 (2)	0 (1)	4 (2)
C(11)	1045 (1)	4055 (3)	1650 (1)	21 (1)	117 (5)	28 (1)	2 (2)	0 (1)	6 (2)
C(12)	305 (1)	4258 (3)	1445 (2)	23 (1)	144 (6)	29 (1)	14 (2)	-1 (1)	4 (2)
C(13)	-226 (1)	3201 (4)	1637 (1)	18 (1)	183 (6)	27 (1)	4 (2)	-1 (1)	-5 (2)
C(14)	-19 (1)	1977 (4)	2041 (2)	22 (1)	166 (6)	34 (1)	-20 (2)	0 (1)	-2 (2)
C(15)	723 (1)	1772 (3)	2252 (1)	26 (1)	124 (5)	28 (1)	-10 (2)	-3 (1)	9 (2)
C(16)	1738 (1)	2640 (3)	3550 (1)	20 (1)	123 (5)	21 (1)	-3 (2)	-4 (1)	6 (2)
C(17)	1414 (2)	4012 (3)	3703 (2)	32 (1)	125 (5)	32 (1)	1 (2)	-3 (1)	5 (2)
C(18)	940 (2)	4094 (4)	4306 (2)	36 (1)	163 (6)	38 (1)	13 (3)	-5 (1)	-18 (2)
C(19)	803 (2)	2861 (4)	4739 (1)	32 (1)	206 (7)	25 (1)	3 (3)	-2 (1)	-6 (2)
C(20)	1138 (2)	1519 (4)	4578 (1)	32 (1)	184 (6)	24 (1)	-15 (2)	0 (1)	10 (2)
C(21)	1614 (2)	1393 (3)	3978 (2)	30 (1)	120 (5)	28 (1)	-5 (2)	-1 (1)	7 (2)
H(5)	1894 (12)	1597 (27)	938 (12)	4.4 (7)					
H(6)	2772 (12)	1608 (27)	-10 (12)	4.9 (7)					
H(7)	4000 (14)	2536 (33)	-11 (15)	7.4 (8)					
H(8)	4350 (14)	3531 (32)	1215 (16)	8.2 (9)					
H(9)	3484 (11)	3556 (23)	2132 (10)	2.6 (6)					
H(11)	1415 (12)	4840 (27)	1517 (12)	4.2 (7)					
H(12)	189 (13)	5213 (30)	1174 (13)	6.4 (8)					
H(13)	-751 (12)	3384 (27)	1476 (13)	4.6 (7)					
H(14)	-366 (13)	1302 (28)	2151 (12)	5.1 (7)					
H(15)	884 (13)	922 (25)	2542 (14)	4.7 (7)					
H(17)	1490 (13)	4888 (28)	3388 (12)	4.6 (7)					
H(18)	696 (14)	5063 (31)	4413 (14)	7.1 (8)					
H(19)	470 (13)	3004 (29)	5171 (14)	6.6 (8)					
H(20)	1031 (15)	715 (31)	4951 (15)	8.0 (9)					
H(21)	1858 (12)	441 (28)	3855 (12)	5.0 (7)					

lity of 0.990. *E*-maps were calculated corresponding to both phases of the symbolic sign. One map contained 18 of the 21 anticipated atoms in a chemically reasonable arrangement whereas the other map contained only random peaks. The coordinates and isotropic temperature factors of these 18 atoms (all considered to be carbon atoms) were refined by block-diagonal least-squares calculations using $1/\sigma^2$ weights, to an $R=0.36$. An electron-density map phased by these atoms revealed the missing three atoms. Further isotropic least-squares refinement on a model in which all 21 atoms were assigned their proper scattering factors reduced the value of the reliability index to $R=0.18$.

The coordinates of the 15 phenyl hydrogen atoms were easily located from a difference electron-density map. These were then included in the atom list and refinement was continued varying the coordinates and

isotropic temperature factors of all 36 atoms. The isotropic temperature factors of the non-hydrogen atoms were then converted to anisotropic temperature factors and refinement was continued until convergence was reached at $R=0.047$ [Stewart, Davidson & Simpson, (1965); Cromer & Waber (1965); for the hydrogen and non-hydrogen scattering factor curves, respectively]. The shifts of all parameters were less than one-tenth of their respective estimated standard deviations and all further attempts at refinement were therefore terminated. A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. 30023.*

* Copies of this table may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England

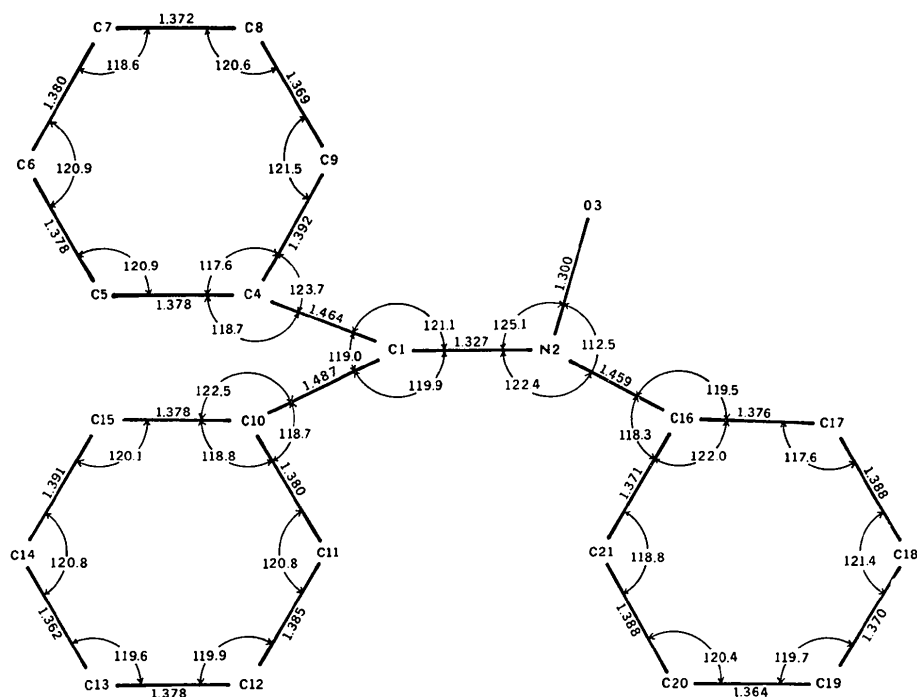


Fig. 2. Schematic drawing of the molecule with distances and angles indicated.

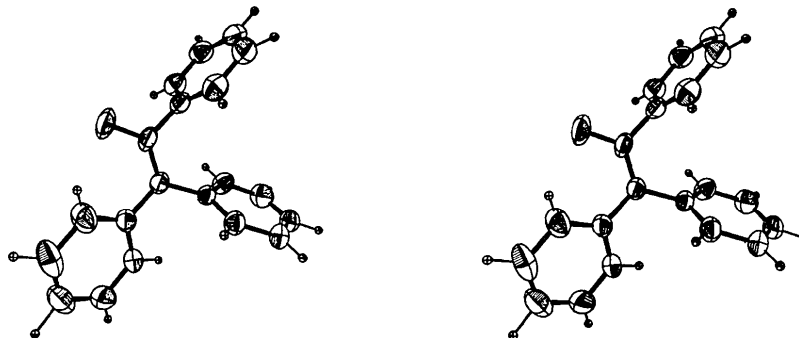


Fig. 3. ORTEP stereo-drawing.

Results and discussion

The final least-squares coordinates and temperature factors for all atoms are listed in Table 1. A schematic drawing of the molecule with bond distances and angles indicated is shown in Fig. 2. The estimated standard deviations (e.s.d.'s) are less than 0.005 Å and 0.3° for non-hydrogen bond distances and angles respectively. The calculated e.s.d.'s involving a hydrogen atom are less than 0.03 Å for bond distances and 1.5° for bond angles.

The internal consistency of the structure determination can be measured by the parameters within the three independent phenyl rings. The average carbon-carbon distance is 1.378 ± 0.007 Å and the average C-C-C bond angle is $120.0 \pm 1.0^\circ$ in agreement with the accepted literature values 1.397 Å and 120.0° respectively. Furthermore, a least-squares fit of each phenyl ring to a best plane shows that each ring is planar with e.s.d.'s of less than 0.004 Å.

That the molecule does exist as a nitron and not as an oxaziridine is apparent in both the ORTEP stereo drawing (Johnson, 1965), Fig. 3, and the bond distances and angles about the CNO moiety. For convenience, the distances and angles about the CNO moiety of this study are compared with those of the previous nitron and oxaziridine structures in Table 2. The C(1)-N(2) bond distance, 1.327 Å, is only slightly longer than the same distance, 1.31 Å, for the nitron (Folting, Jerslev & Lipscomb, 1964) and considerably shorter than the corresponding distance in an oxaziridine derivative (Jerslev, 1967). The N(2)-O(3) distance, 1.300 Å, parallels the previously studied nitron distance 1.28 Å. The C(1)-N(2)-O(3) angle 125.1° indicates that the N-O bond is directed away from the carbon rather than towards it and implies that cyclization might be even more difficult than normally expected.

Table 2. Comparison of distances and angles about the nitron moiety

	This study	Nitron*	Oxaziridine†
C-N	1.327 Å	1.309 Å	1.44 Å
C-O	2.330	2.302	1.43
N-O	1.300	1.284	1.50
C-N-O	125.1°	125.2°	58.4°
N-O-C	27.8	27.1	58.4
O-C-N	27.1	27.1	63.2

* Folting, Jerslev & Lipscomb (1964).

† Jerslev (1967).

The nitron, together with the bonding carbon atoms of the phenyl rings [C(1), N(2), O(3), C(4), C(10), and C(16)], is planar to within 0.03 Å. The dihedral angles between planes containing these atoms are tabulated in Table 3. It is obvious that no one atom causes the small deviation from planarity of this group, although the two α -carbon atoms are tilted slightly out of plane, by approximately 3°. The phenyl rings are not aligned

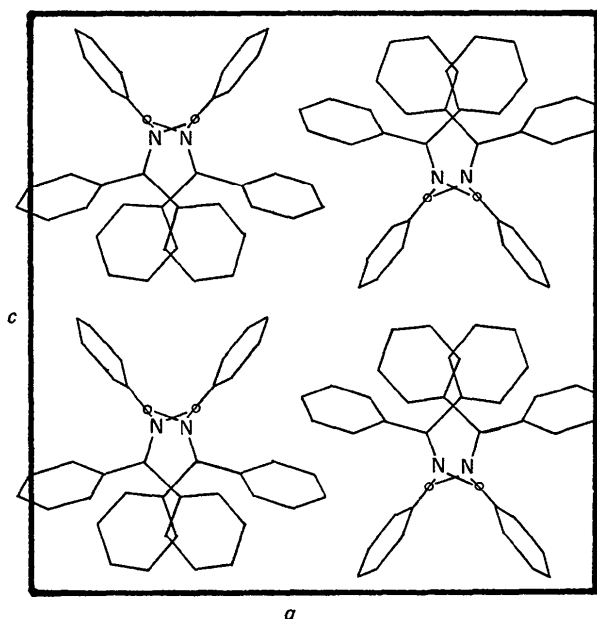


Fig. 4. Unit-cell contents projected down (010).

parallel to the nitron moiety and thus preclude any appreciable delocalization of the aromatic system into the nitron though the phenyl-C distances, 1.464 and 1.487 Å, are slightly shorter than typical aliphatic phenyl substituted derivatives (Takwale & Pant, 1971). These distances parallel the results found in the previous nitron and oxaziridine studies, 1.464 and 1.469 Å respectively.

Table 3. Dihedral angles about bonds in the nitron moiety

Plane no.	Atoms	Dihedral angles with other planes		
		1	2	3
1	C(1), N(2), O(3)			
2	C(1), C(4), C(10)	2.6°		
3	C(1), N(2), C(16)	0.8	3.4°	
4	O(3), N(2), C(16)	0.7	3.2	0.7°

Both previous studies used *N*-methyl substituents rather than the phenyl ring used in this study. For the nitron, the *N*-methyl bond distance, 1.501 Å, was found to be only slightly longer than values reported for three-covalent nitrogen (1.472 Å). In the oxaziridine, although the corresponding distance was rather short, 1.43 Å, no attendant explanation was advanced. In this study, the *N*-phenyl distance lies intermediate (1.459 Å) between these two values. This is slightly longer than the C-N distances found in anilines, 1.41 Å (Sakuri, Sundaralingam & Jeffery, 1963) and 1.43 Å (Christensen & Strømme, 1969), and precludes any abnormal amount of delocalization above that normally expected in *N*-phenyl analogues.

Fig. 4 shows the contents of the unit cell projected

down (010). There are only two non-hydrogen intermolecular contact distances less than 3.5 Å: C(13)–O(3) at 3.36 Å and C(17)–O(3) at 3.28 Å.

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Structure Cristalline du Tetracuprichlorure de Triéthylammonium, [(C₂H₅)₃NH]₂CuCl₄

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The crystal structure of [(C₂H₅)₃NH]₂CuCl₄ has been determined by X-ray diffraction techniques. The crystals are monoclinic, space group *P*2₁/*c*, with *a* = 12.878, *b* = 13.079, *c* = 12.227 Å, β = 97.85°. There are four molecules in the unit cell. The intensities of 1883 reflexions were collected with a Hilger four-circle diffractometer. The structure was solved by direct methods and refined to a final *R* value of 0.064 for the 1655 observed reflexions. The hydrogen atoms were not included in the calculation. The structure of the CuCl₄²⁻ ion is that of a squashed tetrahedron, with Cl–Cu–Cl bond angles equal to 135 and 98°. There is a N–H···Cl hydrogen bond between the tetrachlorocuprate anion and the organic cation (N···Cl = 3.11 Å).

Introduction

L'ion CuCl⁻, existant dans un grand nombre de composés, peut présenter plusieurs configurations différentes, dont les deux plus fréquentes sont, d'une part, une véritable coordination 4 avec une structure quasi-tétraédrique, comme dans Cs₂CuCl₄ (Helmholz & Kruh, 1952) et d'autre part, un entourage plan-carré éventuellement complété par deux autres liaisons plus longues, l'ensemble formant un octaèdre allongé, comme dans (NH₄)₂CuCl₄ (Willett, 1964).

Dans la série des composés de formule générale [(C_nH_{2n+1})_xNH_{4-x}]₂CuCl₄, ces deux types de configuration de l'ion CuCl₄²⁻ sont représentés, le premier dans [(CH₃)₄N]₂CuCl₄ (Morosin & Lingafelter, 1961), le second dans (CH₃NH₂)₂CuCl₄ (Willett, 1964) et (C₂H₅NH₂)₂CuCl₄ (Steadman & Willet 1970).t

Une première étude diffractométrique de la maille d'autres composés de ce groupe a déjà été publiée (Lamotte-Brasseur, 1972) et il nous a paru intéressant de voir comment évolue la coordination du Cu entre les deux cas extrêmes de la série.

Données expérimentales

La méthode générale de préparation des cristaux de cette série a été décrite par Remy & Laves (1933). Les

monocristaux ont été obtenus par évaporation d'un mélange stoechiométrique de (C₂H₅)₃NHCl et CuCl₂·2H₂O en solution dans l'eau.

Les données cristallographiques sont reprises dans le Tableau 1. Les intensités de 1833 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre à quatre cercles Hilger–Watts; parmi celles-ci, 1655 ont été considérées comme observées [*I* > 2(*I*)]. Les principales caractéristiques des mesures sont reprises dans le Tableau 2.

Tableau 1. *Données cristallographiques*

[(C ₂ H ₅) ₃ NH] ₂ CuCl ₄	
Monoclinique	<i>V</i> = 2059,4 Å ³
<i>P</i> 2 ₁ / <i>c</i>	λ(Cu Kα) = 1,5418 Å
<i>a</i> = 12,878 (3) Å	<i>D</i> _m = 1,33 g cm ⁻³
<i>b</i> = 13,079 (3)	<i>D</i> _x = 1,30 g cm ⁻³
<i>c</i> = 12,227 (3)	<i>F</i> ₀₀₀ = 860
<i>Z</i> = 4	μ = 60,1 cm ⁻¹
	Masse moléculaire: 409,5

Tableau 2. *Caractéristiques des mesures*

Rayonnement	Cu Kαλ = 1,5418 Å
Balayage ω/2θ	θ < 55° 70 pas
Temps de mesure du fond continu	14 sec
Temps de mesure d'un pas	1 sec
Compteur à scintillation.	
Dimensions du cristal	0,2 × 0,2 × 0,2 mm