

- LOSCALZO, J., KALLEN, R. G. & VOET, D. (1973). *Arch. Biochem. Biophys.* **157**, 426–430.
- PARTHASARATHY, R., PAUL, B. & KORYTNYK, W. (1976). *J. Am. Chem. Soc.* **98**, 6634–6643.
- RACHINSKII, F. YU. (1964). *Akad. Nauk SSSR*, **4**, 256–264.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Cambridge, England.
- THOMSON, J. F. (1962). *Radiation Protection in Mammals*, p. 84. New York: Reinhold.
- UMARANI, R. (1988). PhD thesis, Anna Univ., Madras, India.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WILSON, G. E. JR & BAZZONE, T. J. (1974). *J. Am. Chem. Soc.* **96**, 1465–1470.
- YAKOVLEV, V. G. (1963). *Chemical Protection of the Body Against Ionising Radiation*, edited by V. S. BALABUKHA. New York: Pergamon Press.

Acta Cryst. (1991). **C47**, 173–176

Structure of *exo* and *endo* Adducts of 1-(*p*-Methoxyphenyl)-2-phenyl-4-trimethylsiloxy-1,2,3,5,6,7,8,8a-octahydroquinoline

BY P. CHARPIN, M. LANCE, M. NIERLICH AND D. VIGNER
CEN/Saclay, SCM, 91191 Gif sur Yvette CEDEX, France

AND L. LE COZ AND L. WARTSKI

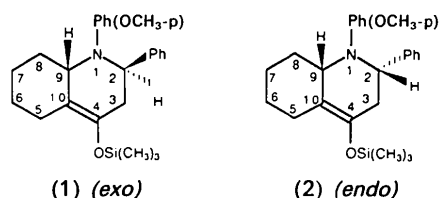
ICMO, Laboratoire des Carbocycles, CNRS-URA 478, Bâtiment 420, 91405 Orsay CEDEX, France

(Received 20 March 1989; accepted 4 June 1990)

Abstract. (1) $C_{25}H_{33}NO_2Si$, $M_r = 407.63$, monoclinic, $P2_1$, $a = 6.018$ (2), $b = 8.073$ (3), $c = 24.205$ (4) Å, $\beta = 92.07$ (2)°, $V = 1175$ (1) Å³, $Z = 2$, $D_x = 1.152$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.1143$ mm⁻¹, $F(000) = 440$, $T = 295$ K, final $R = 0.080$ for 608 unique reflections [$I > 2\sigma(I)$]. (2) $C_{25}H_{33}NO_2Si$, $M_r = 407.63$, triclinic, $P\bar{1}$, $a = 9.106$ (3), $b = 10.541$ (4), $c = 13.210$ (3) Å, $\alpha = 79.20$ (2)°, $\beta = 73.04$ (2)°, $\gamma = 88.06$ (3)°, $V = 1191$ (1) Å³, $Z = 2$, $D_x = 1.137$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.1127$ mm⁻¹, $F(000) = 440$, $T = 295$ K, final $R = 0.076$ for 1188 unique reflections [$I > 3\sigma(I)$]. In both diastereoisomers the cyclohexane ring adopts a chair conformation, while the heterocycle prefers a quasi 1,2-diplanar conformation. They essentially differ in the relative configuration of the C(2)—H(2) and C(9)—H(9) bonds. The structural data are in good agreement with previous data obtained by ¹H NMR. There are no unusual bond lengths or angles.

Introduction. The isolation of the two diastereoisomers of the trimethylsilanol ether adduct obtained by imino Diels–Alder reaction has important mechanistic implications. ¹H NMR gave information only on the position of the phenyl group substituent on C(2): this group lies in quasi axial position in (1), and quasi equatorial position in (2); moreover, in both diastereoisomers, the H(9) proton occupies an axial position in the cyclohexane ring which itself adopts a chair conformation. Unambiguous assignment of

their structures has to be obtained from a single-crystal X-ray structure analysis.



We have previously reported (Le Coz, Wartski, Seyden-Penne, Charpin & Nierlich, 1989) isolation and ¹H NMR results on these silanol ethers.

Experimental. Data collected on an Enraf–Nonius CAD-4 diffractometer, graphite monochromator; cell parameters determined by least squares from the setting angles of 25 reflections ($8 \leq \theta \leq 12^\circ$); three standard reflections measured every 60 min [(1) $\bar{1}0\bar{1}$, $\bar{1}\bar{1}\bar{3}$, 020; (2) $\bar{3}\bar{1}1$, 330, $\bar{3}\bar{3}1$], showed no significant deviation from mean intensity; ω – 2θ scan, ω -scan width: $(0.8 + 0.35 \tan \theta)^\circ$; Lorentz–polarization corrections applied; MicroVAXII computer with SDP (Frenz, 1985) and MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) programs; scattering factors and anomalous components f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1), H atoms included using a riding model

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for non-H atoms of (1)

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$				
	x	y	z	B_{eq}/B_{iso}
Si	0.2295 (8)	0.692	0.5857 (2)	4.1 (1)*
O(1)	0.396 (1)	0.661 (1)	0.6396 (3)	3.1 (2)
O(2)	0.060 (2)	0.037 (1)	0.9709 (4)	4.9 (3)
N(1)	0.246 (2)	0.367 (2)	0.7747 (5)	3.7 (3)
C(2)	0.233 (2)	0.558 (2)	0.7820 (6)	3.2 (4)
C(3)	0.195 (2)	0.630 (2)	0.7250 (5)	3.3 (3)
C(4)	0.353 (2)	0.570 (2)	0.6845 (6)	3.8 (4)
C(5)	0.653 (2)	0.366 (2)	0.6578 (6)	3.7 (4)
C(6)	0.606 (3)	0.185 (2)	0.6354 (6)	5.2 (4)
C(7)	0.566 (2)	0.074 (2)	0.6857 (6)	4.8 (4)
C(8)	0.366 (2)	0.134 (2)	0.7180 (6)	4.0 (4)
C(9)	0.438 (2)	0.312 (2)	0.7419 (6)	3.5 (4)
C(10)	0.462 (2)	0.423 (2)	0.6931 (6)	4.1 (4)
C(11)	0.193 (2)	0.283 (2)	0.8229 (5)	2.4 (3)
C(12)	0.342 (2)	0.166 (2)	0.8496 (6)	4.0 (4)
C(13)	0.290 (2)	0.086 (2)	0.8981 (5)	3.3 (4)
C(14)	0.091 (2)	0.115 (2)	0.9203 (5)	3.1 (4)
C(15)	-0.061 (2)	0.224 (2)	0.8970 (5)	3.1 (3)
C(16)	-0.010 (2)	0.305 (2)	0.8478 (5)	3.1 (4)
C(20)	-0.139 (2)	0.070 (2)	0.9987 (7)	6.4 (5)
C(21)	0.437 (2)	0.626 (2)	0.8144 (5)	3.0 (3)
C(22)	0.454 (2)	0.593 (2)	0.8703 (6)	3.7 (4)
C(23)	0.633 (2)	0.651 (2)	0.9010 (6)	4.6 (4)
C(24)	0.796 (3)	0.757 (2)	0.8780 (7)	5.1 (4)
C(25)	0.766 (2)	0.794 (2)	0.8220 (6)	4.7 (4)
C(26)	0.594 (2)	0.729 (2)	0.7914 (6)	3.7 (4)
C(31)	0.405 (3)	0.790 (2)	0.5336 (6)	6.0 (5)
C(32)	0.121 (3)	0.489 (3)	0.5601 (7)	7.0 (5)
C(33)	0.002 (3)	0.837 (3)	0.6020 (7)	7.6 (5)

*Si atom only refined anisotropically.

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for non-H atoms of (2)

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$				
	x	y	z	B_{eq}/B_{iso}
Si	0.2981 (4)	0.1220 (4)	0.3356 (3)	4.83 (7)*
O(1)	0.3057 (6)	0.0649 (6)	0.2466 (4)	5.1 (2)*
O(2)	0.2951 (8)	0.4323 (7)	-0.4834 (5)	7.9 (2)*
N(1)	0.3061 (7)	0.2768 (6)	-0.0558 (5)	3.9 (2)*
C(2)	0.4475 (3)	0.2103 (3)	-0.0455 (2)	4.3 (2)
C(3)	0.4470 (9)	0.1876 (8)	0.0719 (6)	4.4 (2)
C(4)	0.2972 (9)	0.1329 (8)	0.1472 (6)	4.2 (2)
C(5)	0.024 (1)	0.0584 (9)	0.1836 (7)	5.7 (2)
C(6)	-0.114 (1)	0.1429 (9)	0.1929 (7)	6.3 (3)
C(7)	-0.122 (1)	0.2103 (9)	0.0826 (7)	6.1 (2)
C(8)	0.028 (1)	0.2855 (9)	0.0175 (7)	5.4 (2)
C(9)	0.1658 (9)	0.2003 (8)	0.0071 (6)	4.1 (2)
C(10)	0.1711 (9)	0.1301 (8)	0.1152 (6)	4.0 (2)
C(11)	0.3066 (9)	0.3181 (8)	-0.1662 (6)	3.7 (2)
C(12)	0.321 (1)	0.2300 (9)	-0.2365 (7)	5.2 (2)
C(13)	0.314 (1)	0.2742 (9)	-0.3413 (7)	5.9 (2)
C(14)	0.300 (1)	0.4033 (8)	-0.3779 (7)	5.0 (2)
C(15)	0.2861 (9)	0.4899 (8)	-0.3102 (6)	4.6 (2)
C(16)	0.2892 (9)	0.4446 (8)	-0.2048 (6)	4.3 (2)
C(20)	0.281 (1)	0.561 (1)	-0.5257 (9)	8.9 (3)
C(21)	0.5947 (9)	0.2857 (8)	-0.1149 (6)	3.8 (2)
C(22)	0.610 (1)	0.4144 (8)	-0.1122 (6)	4.9 (2)
C(23)	0.748 (1)	0.4810 (9)	-0.1666 (7)	5.8 (2)
C(24)	0.864 (1)	0.4179 (9)	-0.2248 (7)	5.6 (2)
C(25)	0.852 (1)	0.2982 (9)	-0.2332 (7)	6.0 (2)
C(26)	0.715 (1)	0.2274 (9)	-0.1788 (7)	5.3 (2)
C(31)	0.311 (1)	-0.025 (1)	0.4526 (8)	7.9 (3)
C(32)	0.118 (1)	0.203 (1)	0.4019 (8)	8.1 (3)
C(33)	0.461 (1)	0.2331 (9)	0.3331 (7)	6.1 (3)

* Atoms refined anisotropically.

(C—H 0.95 Å); full-matrix least-squares refinements based on F_o ; no absorption correction. (1): Crystal approximately 0.30 × 0.25 × 0.10 mm, data collected for $1 \leq \theta \leq 22^\circ$ in the index range h 0→6, k 0→8, l -25→25; 1756 independent reflections of which 608 had $I > 2\sigma(I)$; minimized function: $\sum w(\Delta F)^2$, with $w = 1/(\sigma F)^2 = 4F^2/[\sigma^2 F^2 + (pF^2)^2]^{1/2}$, $p = 0.6$; final R values: $R_F = 0.080$, $wR_F = 0.071$, $S = 1.87$; max. shift/e.s.d. = 0.01, highest peak in the final difference Fourier map = 0.33 e Å⁻³. (2): Crystal approximately 0.35 × 0.20 × 0.20 mm, data collected for $1 \leq \theta \leq 25^\circ$ in the index range h -10→10, k 0→12, l -15→15; 4186 independent reflections of which 1188 had $I > 3\sigma(I)$; minimized function: $\sum w(\Delta F)^2$, unit weights; final R values: $R_F = 0.076$, $wR_F = 0.082$, $S = 2.09$; max. shift/e.s.d. = 0.19, final $\Delta\rho_{max} = 0.35$ e Å⁻³. The rather high R values of both compounds are due to poor crystal quality.

Discussion. Final atomic parameters with their B_{eq} values are given in Tables 1 and 2* for (1) and (2), respectively. Comparative selected distances and angles for both compounds are reported in Table 3.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all bond lengths and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52910 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Figs. 1 and 2 show ORTEP drawings of the molecule and packing for (1); Figs. 3 and 4 give the same views for (2).

The conformation of the cyclohexane ring (ring *A*) for both diastereoisomers is a chair, while the heterocyclic ring *B* prefers a quasi 1,2-diplanar conformation, as can be seen from the torsion angles given in Table 3. The relative configuration of the C(2)—H(2) and C(9)—H(9) bonds is *trans* (*exo*) for (1) and *cis* (*endo*) for (2). This can be seen either from the distances to the plane C(2)—N(1)—C(9) of the four atoms H(2), H(9), C(21) and C(11), -0.05, -0.82, -1.27, -0.83 Å (1) and 0.78, 0.89, 1.07, 0.07 Å (2), respectively, or from the pseudo-torsional angle H(2)—C(2)⋯C(9)—H(9), -109 (2) (1) and -16.0 (5)° (2).

The N-atom geometry given by angles in Table 3 is essentially tetrahedral rather than planar in both compounds.

The dihedral angles between the *N*-phenyl plane and the best plane for ring *B* are different, 30.8 (8) and 87.8 (3)° for compounds (1) and (2), respectively. The dihedral angles between the C(2)-phenyl plane and the same heterocyclic ring are comparable [90.6 (4) and 84.0 (3)°] but the C(2)-phenyl group occupies a quasi axial position in (1) and a quasi equatorial position in (2), as shown by the torsional angles H(2)—C(2)—C(3)—H(3*A*) and H(2)—C(2)—C(3)—H(3*B*), -56.1 and 63.0° in (1) and 169.3 and 50.2° in (2).

Table 3. *Interatomic distances (Å), angles (°) and torsion angles (°) for (1) and (2)*

	(1)	(2)
Si—O(1)	1.634 (9)	1.646 (6)
Si—C(31)	1.85 (1)	1.84 (1)
Si—C(32)	1.86 (2)	1.82 (1)
Si—C(33)	1.86 (2)	1.84 (1)
O(1)—C(4)	1.35 (2)	1.39 (1)
O(2)—C(14)	1.40 (2)	1.38 (1)
O(2)—C(20)	1.42 (2)	1.39 (1)
N(1)—C(2)	1.55 (2)	1.474 (7)
N(1)—C(9)	1.49 (2)	1.474 (9)
N(1)—C(11)	1.40 (2)	1.44 (1)
C(2)—C(3)	1.51 (2)	1.52 (1)
C(3)—C(4)	1.47 (2)	1.49 (1)
C(4)—C(10)	1.37 (2)	1.34 (1)
C(5)—C(16)	1.58 (2)	1.50 (1)
C(5)—C(10)	1.53 (2)	1.51 (1)
C(6)—C(7)	1.54 (2)	1.52 (1)
C(7)—C(8)	1.54 (2)	1.53 (1)
C(2)—C(9)	1.60 (2)	1.51 (1)
C(9)—C(10)	1.49 (2)	1.49 (1)
Si—O(1)—C(4)	126.7 (8)	128.2 (5)
C(2)—N(1)—C(9)	113 (1)	109.1 (4)
C(2)—N(1)—C(11)	112 (1)	112.8 (5)
C(9)—N(1)—C(11)	120 (1)	110.8 (7)
N(1)—C(2)—C(3)	107 (1)	109.1 (4)
C(2)—C(3)—C(4)	114 (1)	112.4 (7)
C(3)—C(4)—C(10)	120 (1)	122.1 (7)
N(1)—C(9)—C(8)	105 (1)	109.9 (6)
N(1)—C(9)—C(10)	110 (1)	114.2 (7)
C(8)—C(9)—C(10)	107 (1)	110.7 (6)
C(9)—C(8)—C(7)	105 (1)	111.9 (7)
C(8)—C(7)—C(6)	112 (1)	111.6 (8)
C(7)—C(6)—C(5)	107 (1)	111.0 (7)
C(6)—C(5)—C(10)	110 (1)	112.4 (7)
C(4)—C(10)—C(9)	125 (1)	121.5 (7)
C(4)—C(10)—C(5)	123 (1)	123.9 (7)
C(9)—C(10)—C(5)	111 (1)	114.7 (8)
C(9)—C(8)—C(7)—C(6)	-65 (1)	56 (1)
C(8)—C(7)—C(6)—C(5)	60 (1)	-54 (1)
C(7)—C(6)—C(5)—C(10)	-55 (1)	52 (1)
C(6)—C(5)—C(10)—C(9)	61 (1)	-52 (1)
C(5)—C(10)—C(9)—C(8)	-65 (1)	-51 (1)
C(10)—C(9)—C(8)—C(7)	65 (1)	-53 (1)
N(1)—C(9)—C(10)—C(4)	11 (2)	-3 (1)
C(9)—C(10)—C(4)—C(3)	-1 (2)	-10 (1)
C(10)—C(4)—C(3)—C(2)	22 (2)	-13 (1)
C(4)—C(3)—C(2)—N(1)	-51 (1)	47 (1)
C(3)—C(2)—N(1)—C(9)	64 (1)	-62 (1)
C(2)—N(1)—C(9)—C(10)	-43 (1)	40 (1)

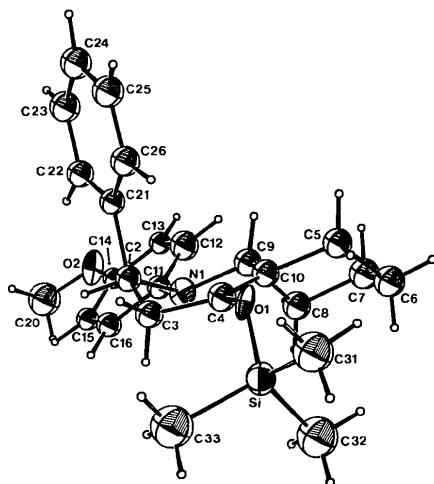


Fig. 1. ORTEP (Johnson, 1976) drawing of (1).

The dihedral angles between the *N*-phenyl ring and the C(2)-phenyl ring are respectively 59.9 (5) and 71.5 (3)°.

The relative position of the trimethylsilyl group to the C(2)-phenyl ring can be observed from their positions on opposite sides of the N(1)—C(9)—C(10)—C(4) plane with Si 1.24 (2) Å out of this plane for both compounds, and very different values for the C(21) distance from this plane, 2.31 (2) in (1) and 0.87 (2) Å in (2).

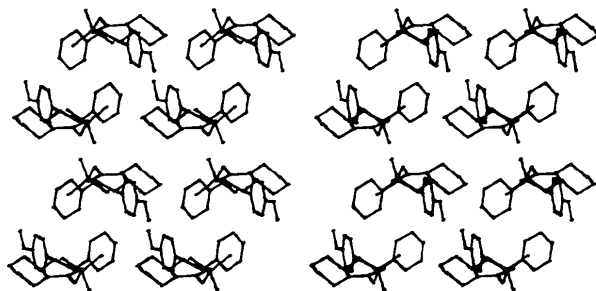


Fig. 2. Stereoscopic view of (1) showing the crystal packing.

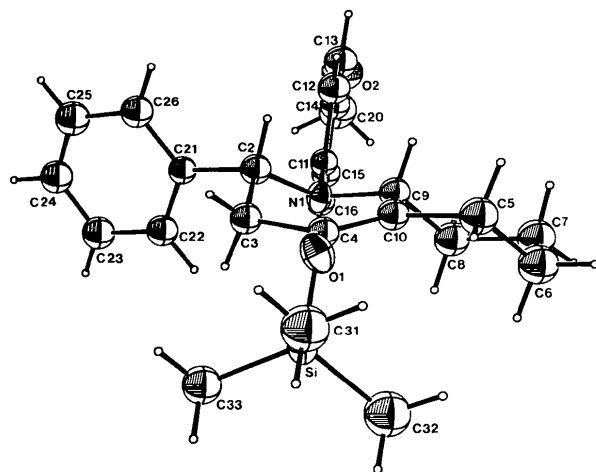


Fig. 3. ORTEP drawing of (2).

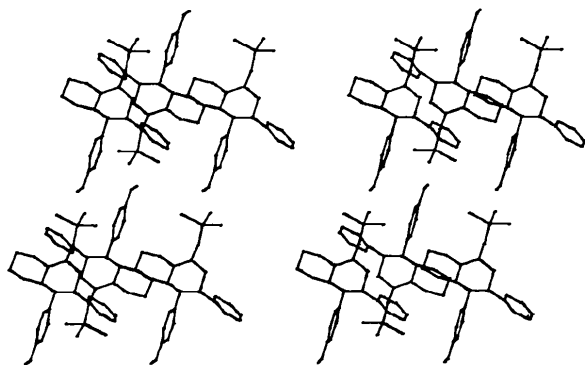


Fig. 4. Stereoscopic view of the crystal packing for (2).

References

- FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LE COZ, L., WARTSKI, L., SEYDEN-PENNE, J., CHARPIN, P. & NIERLICH, M. (1989). *Tetrahedron Lett.* **30**, 2795.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

SHORT-FORMAT PAPERS

Contributions intended for publication under this heading should follow the format given in the Checklist for Authors [Acta Cryst. (1985). C41, 1-4].

Acta Cryst. (1991). **C47**, 176-177

Structure of Nitryl Hexafluoroarsenate(V)

BY HANS PREUT, DIRK BERNSTEIN AND ROLF MINKWITZ

Fachbereich Chemie, Universität Dortmund, Postfach 500500, D-4600 Dortmund, Germany

(Received 28 May 1990; accepted 27 June 1990)

Abstract. NO₂⁺.AsF₆⁻, *M_r* = 234.92, monoclinic, *C2/m*, *a* = 9.053 (2), *b* = 5.790 (2), *c* = 5.077 (2) Å, β = 90.09 (3)°, *V* = 266.1 (2) Å³, *Z* = 2, *D_x* = 2.932 Mg m⁻³, *F*(000) = 220, λ(Mo *Kα*) = 0.71073 Å, μ = 6.45 mm⁻¹, *T* = 291 (1) K, final *R* = 0.021 for 263 unique observed [*F* ≥ 3.0σ(*F*)] diffractometer data. In the crystal, the cation and anion reside on centers of symmetry (2/*m*). The N—O distance in the linear cation is 1.159 (3) Å and the As—F distances in the anion are 1.717 (2) and 1.722 (2) Å. The anion is nearly an ideal octahedron with 180° angles and maximum deviations of 0.5(1)° from the 90° angles. Four symmetrically equivalent F atoms around the nitrogen have a short N⋯F contact of 2.600 (2) Å with O—N⋯F angles between 85.9 (1) and 94.1 (1)° and F⋯N⋯F angles between 80.2 (1) and 99.8 (1)° besides the 180° angles. Through these short N⋯F contacts infinite two-dimensional nets form parallel to *y* and *z* and eight-membered ⋯N⋯F—As—F⋯N⋯F—As—F⋯ heterocycles are formed.

Experimental. Single crystals were prepared from a saturated solution of NO₂⁺.AsF₆⁻ in anhydrous HF at 243 K in a KEL-F reactor equipped with a stainless-steel valve. Over a period of ten days, the HF was removed, stepwise, at this temperature until crystallization began. The solution was then decanted and the crystals dried by pumping out the HF in a high vacuum. Crystal size ~0.09 × 0.12 × 0.12 mm, *D_m* not determined, ω/2θ scan, scan speed

1.50–14.65° min⁻¹ in θ, scan width (1.2 + dispersion)°; Nicolet R3m/V diffractometer equipped with an LT-1 low-temperature device, graphite-monochromated Mo *Kα*; lattice parameters from least-squares fit with 28 reflections up to 2θ = 36.63°; ω scans of low-order reflections along the three crystal axes showed acceptable mosaicity; six standard reflections (200, 040, 002, 200, 040, 002) recorded every 2.5 h, only random deviations over 18.65 h of X-ray exposure; 939 reflections measured, 3.0 ≤ θ ≤ 50.0°, -10 ≤ *h* ≤ 10, -6 ≤ *k* ≤ 6, -6 ≤ *l* ≤ 4; after averaging (*R*_{int} = 0.024): 263 unique reflections, 263 with *F* ≥ 3.0σ(*F*); Lorentz-polarization correction, no absorption correction; systematic absences (*hkl*) *h* + *k* = 2*n* + 1 conform to space groups *C2/m*, *C2* and *Cm*; structure solution in *C2/m* via direct methods, Δ*F* syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all atoms; refinement on *F* with 263 reflections and 30 refined parameters; *w* = 1.0/[σ²(*F*) + (0.000686*F*²)] which led to featureless analysis of variance in terms of sinθ and *F_o*; *S* = 1.046, *R* = 0.021, *wR* = 0.021, (Δ/σ)_{max} = 0.004, no extinction correction; largest peak in final Δ*F* map ±0.5 (1) e Å⁻³; atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV); programs: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987); *PCK83* (Williams, 1984), *PLATON* (Spek, 1982) and *MISSYM* (Le Page, 1987). The anion and cation with the numbering scheme are shown in Fig. 1 and