Supporting Information for

Charge Localization in a Dihydrazine Analogue of Tetramethyl-p-phenylenediamine Radical Cation

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Compound Preparation:

1,4-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-benzene-1,4-diyl. (**2**) Butyllithium (0.95 ml, 2.1 M in hexanes, 2.0 mmole) was added dropwise with stirring to a suspension of 1,4-diiodobenzene (0.33 g, 1.0 mmole) in ether (4 ml), under nitrogen. The mixture turned bright yellow and the precipitate of 1,4-diiodobenzene dissolved. It was stirred for additional 20 minutes and 2-t-Bu-2,3-diazabicyclo[2.2.2]-oct-2-ene iodide (0.59 g, 2.3 mmole) was added to the mixture. After 20 min. the mixture became a thick jelly, and ether (2.5 ml) was added and the mixture was allowed to warm to room temperature and stirred for additional 90 minutes. Water (20 ml) was added and the mixture was extracted with methylene chloride (3×20 ml). The combined extracts were dried over $MgSO_4$, filtered and evaporated to give an oily solid (0.65 g). This material proved too sensitive to air for convenient chromatography. The crude product was dissolved in benzene (5 ml), filtered, evaporated and redissolved in benzene (1 ml). Acetonitrile (*ca* 5 ml) was added to precipitate a white solid, which was filtered, washed with small amount of acetonitrile, and dried under vacuum to gave 184 mg (45 %) of **2**, mp. 203-205 °C. Slow recrystallization by vapor diffusion of acetonitrile into a benzene solution afforded single crystals suitable for x-ray crystallographic analysis which proved the stucture. ^{1}H NMR (500MHz, C_6D_6, room temperature) : d 7.93 (br.s., 2H, Ar-H), 7.01 & 6.88 (2 br.s., 2H, Ar-H), 3.48 (br.s., 2H, NCH), 3.16 (br.s., 2H, NCH), 2.23 (mult., 2H), 2.01 (br.s., 2H), 1.75 (br.m., 4H), 1.50 br.t. (J=11.5 Hz) (2H), 1.39 br.t. (J=12 Hz) (2H), 1.07-1.25 m. (2H), 1.17 s. (18H, CMe_3), 0.95 br.s.

(2H). This spectrum is complicated by being a mixture of both diastereomers, and exhibiting broadening from N-C_{Ar} rotation. ^{13}C NMR (125 MHz, C_6D_6, 80 °C, all peaks are sharp): d 150.34 (N$\underline{C}_{ar}$), 150.25 (N$\underline{C}_{ar}$), 120.57 ($\underline{C}_{ar}H$), 58.68 ($\underline{C}(CH_3)_3$)), 54.95 & 54.71 (N$\underline{C}$H each ½ intensity), 46.66 (N$\underline{C}$H), 29.46 ($\underline{C}H_2$), 29.07 (C($\underline{C}H_3)_3$)), 27.18 ($\underline{C}H_2$), 22.87 ($\underline{C}H_2$), 21.21 ($\underline{C}H_2$). N-C_{Ar} rotation is rapid, but double nitrogen inversion is slow; the only carbons for which the two diastereomers are resolved are N$\underline{C}_{Ar}$ and one set of N$\underline{C}$H carbons. ^{13}C NMR (125 MHz, CD_2Cl_2, -32 °C, aromatic region, all peaks sharp): d 149.40, 149.28, 149.02 (double intensity) (N$\underline{C}_{ar}$); 119.50, 119.39, 119.25, 119.13, 119.06, 118.91, 118.59, 118.23 ($\underline{C}_{ar}H$). N-C_{Ar} rotation is frozen, and peaks for *syn* and *anti* forms of both diastereomers are resolved, with one accidental overlap. MS: found, 410.3422 (int. 36%), calcd for $C_{24}H_{42}N_4$ 410.3095.

1,4-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-benzene-1,4-diyl radical cation tetraphenylborate ($2^+BPh_4^-$).

2 (8.2 mg, 0.020 mmole) was dissolved in CH_2Cl_2 (0.5 ml) and $AgNO_3$ (700 mL, 0.02293 M in CH3CN, 0.016 mmole) was added at 0 °C. The resulting green solution was centrifuged to remove Ag precipitate and $NaBPh_4$ (7.7 mg, 0.0225 mmole in 2 ml of CH_3CN) was added. The solution was evaporated to 0.5 mL and 2 drops of water were added. Water was allowed to diffuse in overnight to give a mixture of dark green plates of $\mathbf{2}^+$ $B(Ph)_4^-$ with colorless crystals of **2** used in excess. The temperature of the solution and was maintained at 0 °C by an ice bath.

2-t-Bu-3-phenyl-2,3-diazabicyclo[2.2.2]octane (**3**). Phenyllithium (2 ml, 4 mmole, 2M in cyclohexane:ether) was added dropwise, under nitrogen, to 2-t-Bu-2,3-diazabicyclo[2.2.2]oct-2-ene tetraflouroborate (441 mg, 1.64 mmole) in ether (6 ml) and the mixture was stirred for 2 hours. Upon quenching with water (25 ml) the mixture was extracted with ether (4×25 ml), dried over $MgSO_4$, and evaporated to give a yellow oil with some solid. The crude product was

filtered through 15 g of silica gel (methylene chloride :pentane = 1:1, Rf=0.9) to give upon evaporation yellow oil (460 mg). Biphenyl impurity was removed by extraction, giving 300 mg (74%) of **3** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): d 7.83 (m, 1H), 7.17 (m, 2H), 6.94 (m, 1H), 6.82 (m, 1H), 3.72 (br.s, 1H), 3.36 (m, 1H), 2.27 (m, 1H), 2.00 - 1.72 (m, 3H), 1.61 (m, 2H); 1.37 (m., 1H), 1.22 (m, 1H), 1.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): d 156.46 (C_q), 127.79 (CH), 120.14 (br., CH), 119.90 (br., CH), 119.77 (br., CH), 58.38 (C_q), 53.92 (CH), 46.25 (CH), 28.79 (CH_2), 26.40 (CH_2), 25.56 (CH_3), 22.13 (CH_2), 21.35 (CH_2). MS: found, 246.1938 (int. 20%), calcd for $C_{16}H_{24}N_2$ 246.1939.

2-t-Bu-3-phenyl-2,3-diazabicyclo[2.2.2]octane radical cation nitrate ($\mathbf{3}^+NO_3^-$).

A solution of **3** 85.0 mg, 0.346 mmole) in acetonitrile (2 ml) was added dropwise, under nitrogen, to silver nitrate (58.5 mg, 0.344 mmole) in acetonitrile (3 ml) that was cooled in an ice/salt bath. The mixture was stirred for 30 min. to give a deeply orange-red solution that was filtered through Celite under nitrogen. The radical cation was precipitated with ether and recrystallized twice by vapor diffusion of ether into acetonitrile and methylene chloride, respectively, giving 61 mg (58%) of orange crystals of $\mathbf{3}^+NO_3^-$ which were used for x-ray crystallographic analysis which proved the structure.

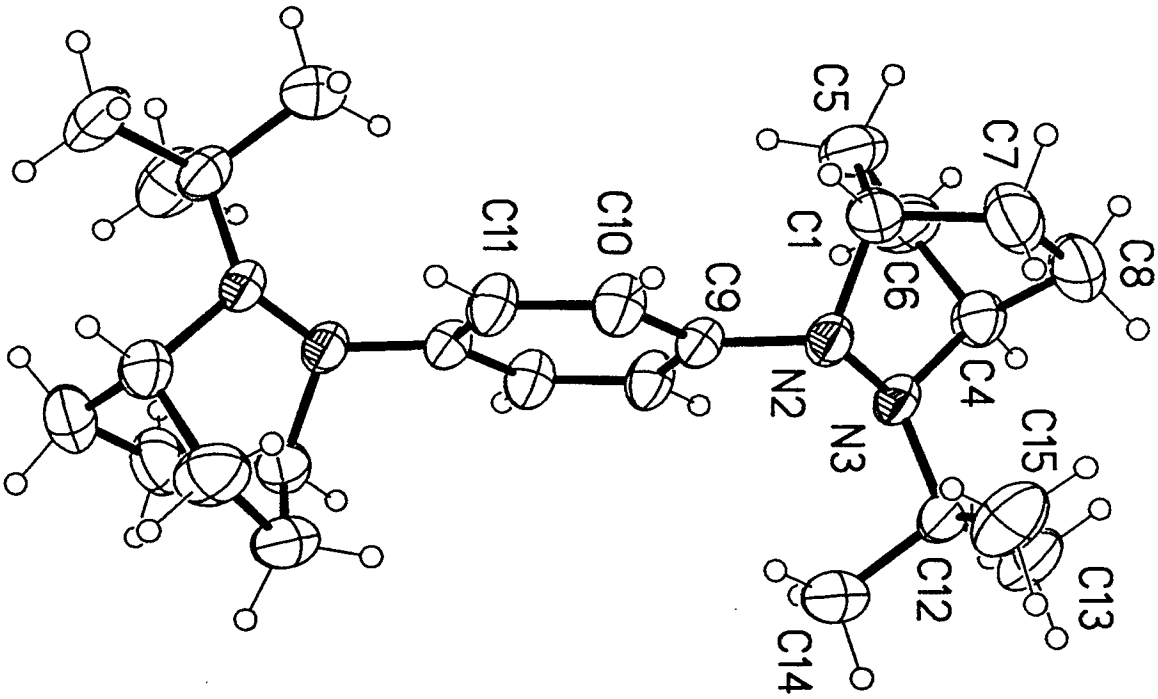
Crystallography.

Intensity data were measured with a Siemens P4/CCD diffractometer using graphite monochromated MoKa radiation (l = 0.71073 Å). Crystal data and refinement parameters are summarized in Table 2. The structures were solved using the SHELXS-86 program and refined using the SHELXS-93 program which refines on F^2 values.

Table 2. Crystal data and structure refinement parameters

compound number	**2**	**2**$^{+}$ $B(Ph)_4^-$	**3**$^{+}$ NO_3^-
empirical formula	$C_{26}H_{42}N_4$	$C_{50}H_{62}N_4B$	$C_{16}H_{24}N_3O_3$
temperature, K	295 (2)	133 (2)	133 (2)
space group	$P\bar{1}$	Pbca	$P2_12_12_1$
Z	1	8	4
a, Å	6.5000 (5)	14.8524 (2)	8.0115 (4)
b, Å	7.2299 (5)	13.9105 (3)	12.8872 (6)
c, Å	13.3764 (10)	40.8752 (2)	15.3184 (7)
a, deg	94.301 (2)	90	90
b, deg	99.039 (2)	90	90
g, deg	105.083 (2)	90	90
Volume, Å^3	594.98 (8)	8445.0 (2)	1581.56 (13)
Density, (calcd), g/cm^3	1.146	1.148	1.287 Mg/m
F(000)	226	3160	660
Crystal size, mm	0.5 x 0.4 x 0.2	0.44 x 0.2 x 0.02	0.4 x 0.2 x 0.1
Reflections collected	3684	26454	4264
Independent reflections [a]	2049 (0.0265)	7058 (0.0679)	2605 (0.0256)
Final R indices [b]	0.0450 / 0.1109	0.0642 / 0.1133	0.0336 / 0.0828
R indices (all data)	0.0524 / 0.1226	0.1097 / 0.1398	0.0361 / 0.0862
Goodness-of-fit on F^2	1.058	1.168	1.073
Data / restraints / parameters	2048 / 0 / 137	7044 / 0 / 497	2605 / 0 / 200
Largest diff map peaks, eÅ^{-3}	0.146 and -0.125	0.236 and - 0.209	0.185 and -0.153

[a] In parenthesis: R_{int}. [b] R_1/wR_2, [I > 2s(I)]. Full-matrix least-squares refinment on F^2.



Thermal Ellipsoid Drawing (50% Probability Level)
of the X-Ray Crystal Structure of **2**.

Table 3. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 2. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	5599(3)	6054(2)	3495(1)	45(1)
N(2)	7312(2)	7656(2)	3222(1)	35(1)
N(3)	8475(2)	6926(2)	2503(1)	35(1)
C(4)	7751(3)	4793(2)	2346(1)	45(1)
C(5)	6646(3)	4673(3)	4049(2)	57(1)
C(6)	8179(4)	4113(3)	3391(2)	60(1)
C(7)	4083(3)	4976(3)	2526(2)	59(1)
C(8)	5342(3)	3979(3)	1889(2)	61(1)
C(9)	8730(2)	8811(2)	4114(1)	34(1)
C(10)	7840(2)	9857(2)	4754(1)	41(1)
C(11)	9071(2)	11014(2)	5630(1)	41(1)
C(12)	8487(3)	8011(2)	1588(1)	45(1)
C(13)	9322(4)	6967(3)	772(1)	61(1)
C(14)	10116(4)	9979(3)	1945(2)	70(1)
C(15)	6316(4)	8332(3)	1125(2)	68(1)

Table 4. Bond lengths [Å] and angles [°] for 2.

C(1)-N(2)	1.494(2)	C(1)-C(7)	1.519(2)
C(1)-C(5)	1.521(3)	N(2)-C(9)	1.440(2)
N(2)-N(3)	1.461(2)	N(3)-C(4)	1.478(2)
N(3)-C(12)	1.503(2)	C(4)-C(6)	1.525(2)
C(4)-C(8)	1.529(3)	C(5)-C(6)	1.537(3)
C(7)-C(8)	1.532(3)	C(9)-C(11)#1	1.387(2)
C(9)-C(10)	1.387(2)	C(10)-C(11)	1.387(2)
C(11)-C(9)#1	1.387(2)	C(12)-C(13)	1.527(2)
C(12)-C(14)	1.526(3)	C(12)-C(15)	1.531(3)

N(2)-C(1)-C(7)	109.14(14)	N(2)-C(1)-C(5)	109.71(13)
C(7)-C(1)-C(5)	109.5(2)	C(9)-N(2)-N(3)	113.07(11)
C(9)-N(2)-C(1)	111.89(12)	N(3)-N(2)-C(1)	111.12(11)
N(2)-N(3)-C(4)	109.83(11)	N(2)-N(3)-C(12)	110.55(11)
C(4)-N(3)-C(12)	118.99(12)	N(3)-C(4)-C(6)	106.80(13)
N(3)-C(4)-C(8)	113.34(14)	C(6)-C(4)-C(8)	108.7(2)
C(1)-C(5)-C(6)	107.32(14)	C(4)-C(6)-C(5)	109.1(2)
C(1)-C(7)-C(8)	108.9(2)	C(4)-C(8)-C(7)	107.55(14)
C(11)#1-C(9)-C(10)	117.57(13)	C(11)#1-C(9)-N(2)	124.78(13)
C(10)-C(9)-N(2)	117.64(13)	C(9)-C(10)-C(11)	121.99(14)
C(9)#1-C(11)-C(10)	120.42(14)	N(3)-C(12)-C(13)	108.78(13)
N(3)-C(12)-C(14)	105.84(13)	C(13)-C(12)-C(14)	108.2(2)
N(3)-C(12)-C(15)	115.85(14)	C(13)-C(12)-C(15)	109.52(14)
C(14)-C(12)-C(15)	108.3(2)		

Symmetry transformations used to generate equivalent atoms:

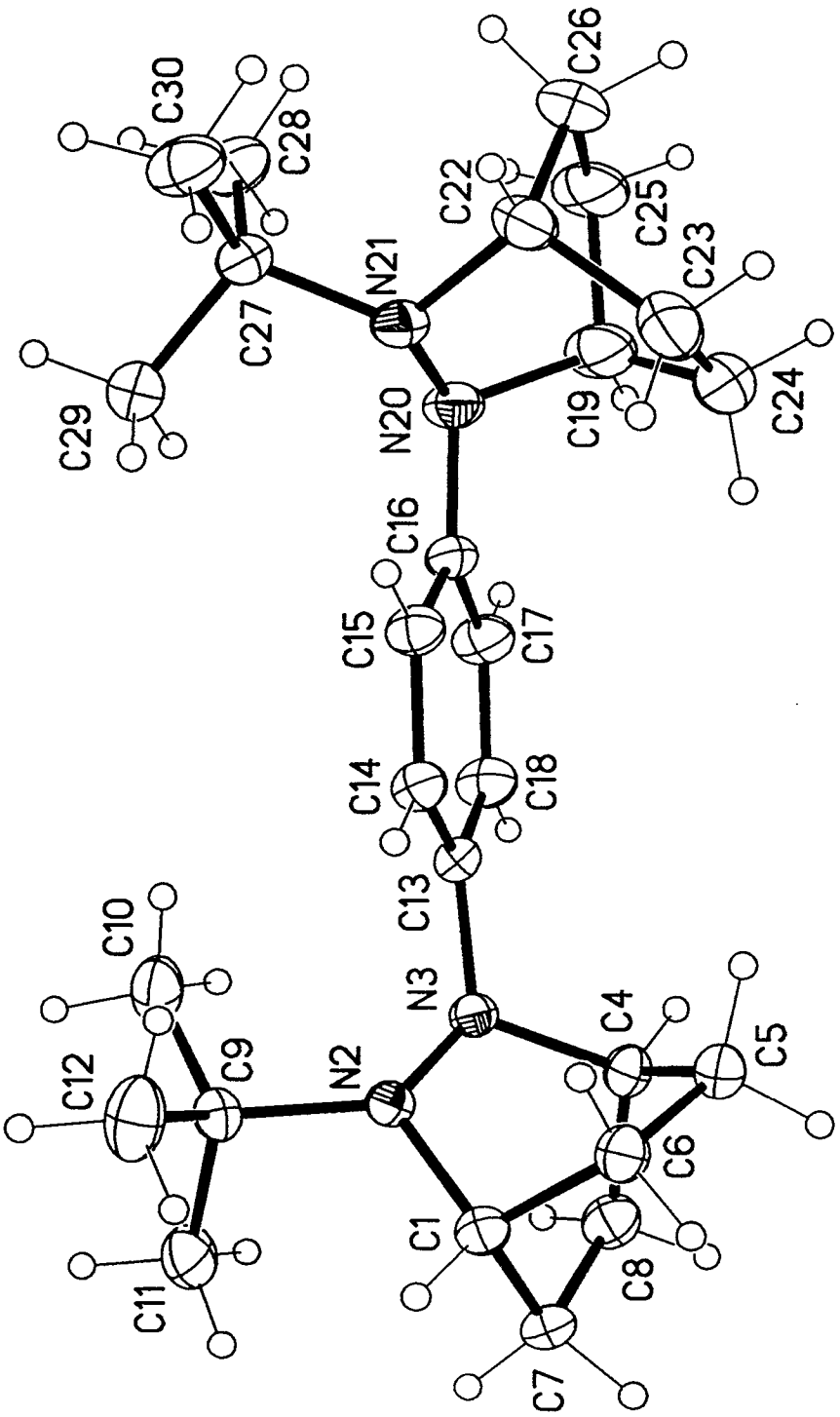
#1 -x+2,-y+2,-z+1

Table 5. Anisotropic displacement parameters [$Å^2$ x 10^3] for 2.

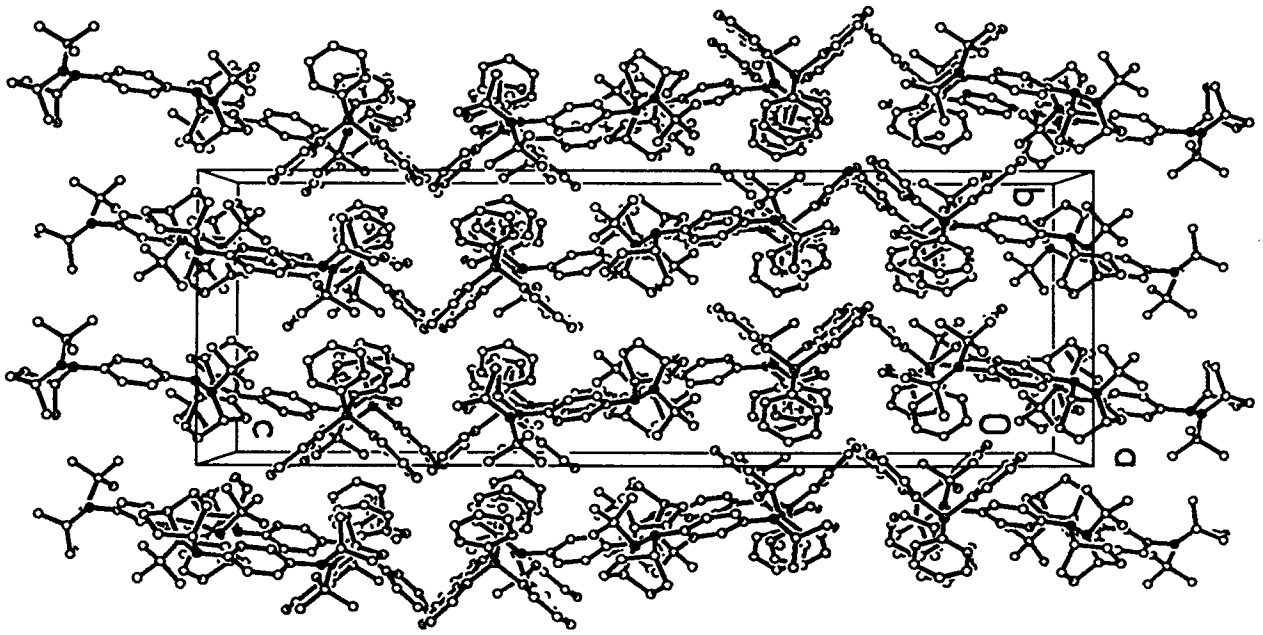
The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	42(1)	46(1)	42(1)	0(1)	13(1)	4(1)
N(2)	37(1)	41(1)	26(1)	-1(1)	6(1)	10(1)
N(3)	43(1)	37(1)	25(1)	-1(1)	8(1)	11(1)
C(4)	59(1)	38(1)	40(1)	0(1)	13(1)	14(1)
C(5)	74(1)	51(1)	48(1)	16(1)	24(1)	13(1)
C(6)	81(1)	54(1)	57(1)	21(1)	23(1)	31(1)
C(7)	46(1)	58(1)	61(1)	-9(1)	6(1)	-1(1)
C(8)	64(1)	47(1)	56(1)	-13(1)	10(1)	-2(1)
C(9)	39(1)	38(1)	24(1)	2(1)	6(1)	10(1)
C(10)	35(1)	51(1)	36(1)	-3(1)	4(1)	14(1)
C(11)	42(1)	50(1)	32(1)	-5(1)	8(1)	16(1)
C(12)	59(1)	49(1)	28(1)	6(1)	9(1)	14(1)
C(13)	80(1)	76(1)	31(1)	8(1)	19(1)	26(1)
C(14)	101(2)	51(1)	51(1)	12(1)	25(1)	-1(1)
C(15)	86(2)	83(2)	46(1)	19(1)	8(1)	42(1)



Thermal Ellipsoid Drawing (50% Probability Level) of the X-Ray Crystal Structure of $2^{+\cdot}$.



Packing Diagram for 2^{+} BPh_4^{-}

Table 6. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 2^+ U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4722(2)	7267(2)	6774(1)	23(1)
N(2)	4986(1)	6630(2)	6500(1)	19(1)
N(3)	5873(1)	6706(2)	6423(1)	19(1)
C(4)	6390(2)	7302(2)	6660(1)	23(1)
C(5)	6020(2)	8326(2)	6638(1)	27(1)
C(6)	4985(2)	8283(2)	6665(1)	25(1)
C(7)	5237(2)	7014(2)	7089(1)	26(1)
C(8)	6235(2)	6879(2)	6999(1)	28(1)
C(9)	4435(2)	5755(2)	6413(1)	21(1)
C(10)	4887(2)	5132(2)	6156(1)	32(1)
C(11)	4333(2)	5166(2)	6727(1)	37(1)
C(12)	3523(2)	6094(2)	6287(1)	37(1)
C(13)	6127(2)	6778(2)	6085(1)	20(1)
C(14)	5563(2)	7205(2)	5858(1)	23(1)
C(15)	5853(2)	7332(2)	5537(1)	24(1)
C(16)	6713(2)	7047(2)	5440(1)	24(1)
C(17)	7263(2)	6593(2)	5673(1)	29(1)
C(18)	6977(2)	6464(2)	5990(1)	27(1)
C(19)	7888(2)	7787(3)	5109(1)	44(1)
N(20)	7048(2)	7189(2)	5117(1)	28(1)
N(21)	6366(2)	7570(2)	4897(1)	25(1)
C(22)	6644(2)	8526(2)	4771(1)	36(1)
C(23)	6826(3)	9156(3)	5071(1)	53(1)
C(24)	7674(3)	8784(3)	5247(1)	61(1)
C(25)	8200(2)	7884(3)	4753(1)	49(1)
C(26)	7504(2)	8486(3)	4564(1)	44(1)
C(27)	6053(2)	6820(2)	4660(1)	26(1)
C(28)	6788(2)	6330(2)	4454(1)	34(1)
C(29)	5593(2)	6031(2)	4861(1)	36(1)
C(30)	5350(2)	7287(2)	4438(1)	37(1)
B(1)	4887(2)	1719(2)	6666(1)	23(1)
C(1A)	4817(2)	994(2)	6349(1)	21(1)
C(2A)	5585(2)	599(2)	6203(1)	26(1)
C(3A)	5554(2)	-37(2)	5942(1)	31(1)
C(4A)	4734(2)	-334(2)	5818(1)	33(1)
C(5A)	3956(2)	11(2)	5962(1)	28(1)
C(6A)	4000(2)	651(2)	6222(1)	25(1)
C(1B)	3951(2)	2343(2)	6717(1)	21(1)
C(2B)	3500(2)	2767(2)	6450(1)	24(1)
C(3B)	2739(2)	3339(2)	6488(1)	27(1)
C(4B)	2394(2)	3524(2)	6796(1)	33(1)
C(5B)	2821(2)	3125(2)	7063(1)	33(1)
C(6B)	3580(2)	2547(2)	7025(1)	28(1)
C(1C)	5682(2)	2540(2)	6623(1)	24(1)
C(2C)	6062(2)	2810(2)	6324(1)	27(1)
C(3C)	6679(2)	3563(2)	6295(1)	33(1)

C(4C)	6937(2)	4080(2)	6568(1)	32(1)
C(5C)	6588(2)	3826(2)	6868(1)	37(1)
C(6C)	5973(2)	3076(2)	6894(1)	32(1)
C(1D)	5094(2)	1005(2)	6977(1)	26(1)
C(2D)	5966(2)	817(2)	7094(1)	36(1)
C(3D)	6136(3)	131(3)	7337(1)	48(1)
C(4D)	5433(3)	-390(2)	7470(1)	47(1)
C(5D)	4569(3)	-221(2)	7364(1)	43(1)
C(6D)	4407(2)	459(2)	7122(1)	32(1)

Table 7. Bond lengths [Å] and angles [°] for 2^+.

C(1)-N(2)	1.479(3)	C(1)-C(6)	1.532(4)
C(1)-C(7)	1.540(4)	N(2)-N(3)	1.359(3)
N(2)-C(9)	1.510(3)	N(3)-C(13)	1.436(3)
N(3)-C(4)	1.487(3)	C(4)-C(8)	1.523(4)
C(4)-C(5)	1.530(4)	C(5)-C(6)	1.542(4)
C(7)-C(8)	1.539(4)	C(9)-C(10)	1.518(4)
C(9)-C(12)	1.524(4)	C(9)-C(11)	1.531(4)
C(13)-C(14)	1.385(4)	C(13)-C(18)	1.391(4)
C(14)-C(15)	1.390(4)	C(15)-C(16)	1.394(4)
C(16)-C(17)	1.404(4)	C(16)-N(20)	1.426(3)
C(17)-C(18)	1.376(4)	C(19)-N(20)	1.499(4)
C(19)-C(24)	1.530(5)	C(19)-C(25)	1.531(4)
N(20)-N(21)	1.454(3)	N(21)-C(22)	1.485(4)
N(21)-C(27)	1.496(3)	C(22)-C(23)	1.529(4)
C(22)-C(26)	1.534(4)	C(23)-C(24)	1.540(5)
C(25)-C(26)	1.540(5)	C(27)-C(30)	1.528(4)
C(27)-C(29)	1.531(4)	C(27)-C(28)	1.540(4)
B(1)-C(1A)	1.644(4)	B(1)-C(1D)	1.644(4)
B(1)-C(1C)	1.652(4)	B(1)-C(1B)	1.652(4)
C(1A)-C(2A)	1.400(4)	C(1A)-C(6A)	1.403(4)
C(2A)-C(3A)	1.386(4)	C(3A)-C(4A)	1.383(4)
C(4A)-C(5A)	1.383(4)	C(5A)-C(6A)	1.388(4)
C(1B)-C(6B)	1.401(4)	C(1B)-C(2B)	1.409(4)
C(2B)-C(3B)	1.390(4)	C(3B)-C(4B)	1.383(4)
C(4B)-C(5B)	1.380(4)	C(5B)-C(6B)	1.394(4)
C(1C)-C(2C)	1.398(4)	C(1C)-C(6C)	1.403(4)
C(2C)-C(3C)	1.396(4)	C(3C)-C(4C)	1.381(4)
C(4C)-C(5C)	1.379(4)	C(5C)-C(6C)	1.390(4)
C(1D)-C(6D)	1.404(4)	C(1D)-C(2D)	1.405(4)
C(2D)-C(3D)	1.399(4)	C(3D)-C(4D)	1.384(5)
C(4D)-C(5D)	1.375(5)	C(5D)-C(6D)	1.388(4)

N(2)-C(1)-C(6)	105.4(2)	N(2)-C(1)-C(7)	111.4(2)
C(6)-C(1)-C(7)	109.1(2)	N(3)-N(2)-C(1)	112.7(2)
N(3)-N(2)-C(9)	122.2(2)	C(1)-N(2)-C(9)	121.2(2)
N(2)-N(3)-C(13)	118.9(2)	N(2)-N(3)-C(4)	113.1(2)
C(13)-N(3)-C(4)	116.8(2)	N(3)-C(4)-C(8)	107.4(2)
N(3)-C(4)-C(5)	107.2(2)	C(8)-C(4)-C(5)	111.1(2)
C(4)-C(5)-C(6)	108.5(2)	C(1)-C(6)-C(5)	108.1(2)
C(8)-C(7)-C(1)	107.8(2)	C(4)-C(8)-C(7)	108.5(2)
N(2)-C(9)-C(10)	112.6(2)	N(2)-C(9)-C(12)	108.1(2)
C(10)-C(9)-C(12)	109.6(2)	N(2)-C(9)-C(11)	106.7(2)
C(10)-C(9)-C(11)	108.6(2)	C(12)-C(9)-C(11)	111.2(2)
C(14)-C(13)-C(18)	119.8(3)	C(14)-C(13)-N(3)	121.1(2)
C(18)-C(13)-N(3)	119.0(2)	C(13)-C(14)-C(15)	119.9(3)
C(14)-C(15)-C(16)	121.0(3)	C(15)-C(16)-C(17)	118.0(3)
C(15)-C(16)-N(20)	122.9(3)	C(17)-C(16)-N(20)	119.1(2)
C(18)-C(17)-C(16)	121.1(3)	C(17)-C(18)-C(13)	120.2(3)
N(20)-C(19)-C(24)	108.7(3)	N(20)-C(19)-C(25)	108.8(3)
C(24)-C(19)-C(25)	109.4(3)	C(16)-N(20)-N(21)	112.3(2)
C(16)-N(20)-C(19)	112.8(2)	N(21)-N(20)-C(19)	111.4(2)
N(20)-N(21)-C(22)	110.3(2)	N(20)-N(21)-C(27)	111.3(2)
C(22)-N(21)-C(27)	119.1(2)	N(21)-C(22)-C(23)	106.6(2)

N(21)-C(22)-C(26)	113.0(3)	C(23)-C(22)-C(26)	108.3(3)
C(22)-C(23)-C(24)	109.0(3)	C(19)-C(24)-C(23)	107.6(3)
C(19)-C(25)-C(26)	108.8(3)	C(22)-C(26)-C(25)	107.5(3)
N(21)-C(27)-C(30)	107.5(2)	N(21)-C(27)-C(29)	107.0(2)
C(30)-C(27)-C(29)	108.6(2)	N(21)-C(27)-C(28)	116.3(2)
C(30)-C(27)-C(28)	110.3(2)	C(29)-C(27)-C(28)	107.0(2)
C(1A)-B(1)-C(1D)	104.5(2)	C(1A)-B(1)-C(1C)	112.7(2)
C(1D)-B(1)-C(1C)	111.4(2)	C(1A)-B(1)-C(1B)	111.7(2)
C(1D)-B(1)-C(1B)	112.1(2)	C(1C)-B(1)-C(1B)	104.6(2)
C(2A)-C(1A)-C(6A)	114.4(3)	C(2A)-C(1A)-B(1)	121.7(2)
C(6A)-C(1A)-B(1)	123.7(2)	C(3A)-C(2A)-C(1A)	123.5(3)
C(4A)-C(3A)-C(2A)	120.1(3)	C(5A)-C(4A)-C(3A)	118.5(3)
C(4A)-C(5A)-C(6A)	120.5(3)	C(5A)-C(6A)-C(1A)	122.9(3)
C(6B)-C(1B)-C(2B)	115.0(3)	C(6B)-C(1B)-B(1)	123.5(3)
C(2B)-C(1B)-B(1)	121.4(2)	C(3B)-C(2B)-C(1B)	122.7(3)
C(4B)-C(3B)-C(2B)	120.5(3)	C(5B)-C(4B)-C(3B)	118.4(3)
C(4B)-C(5B)-C(6B)	121.0(3)	C(5B)-C(6B)-C(1B)	122.3(3)
C(2C)-C(1C)-C(6C)	115.0(3)	C(2C)-C(1C)-B(1)	124.6(3)
C(6C)-C(1C)-B(1)	120.3(3)	C(3C)-C(2C)-C(1C)	122.7(3)
C(4C)-C(3C)-C(2C)	120.3(3)	C(5C)-C(4C)-C(3C)	118.8(3)
C(4C)-C(5C)-C(6C)	120.3(3)	C(5C)-C(6C)-C(1C)	122.9(3)
C(6D)-C(1D)-C(2D)	115.2(3)	C(6D)-C(1D)-B(1)	121.2(3)
C(2D)-C(1D)-B(1)	123.3(3)	C(3D)-C(2D)-C(1D)	122.3(3)
C(4D)-C(3D)-C(2D)	120.1(3)	C(5D)-C(4D)-C(3D)	119.3(3)
C(4D)-C(5D)-C(6D)	120.2(3)	C(5D)-C(6D)-C(1D)	122.9(3)

Symmetry transformations used to generate equivalent atoms:

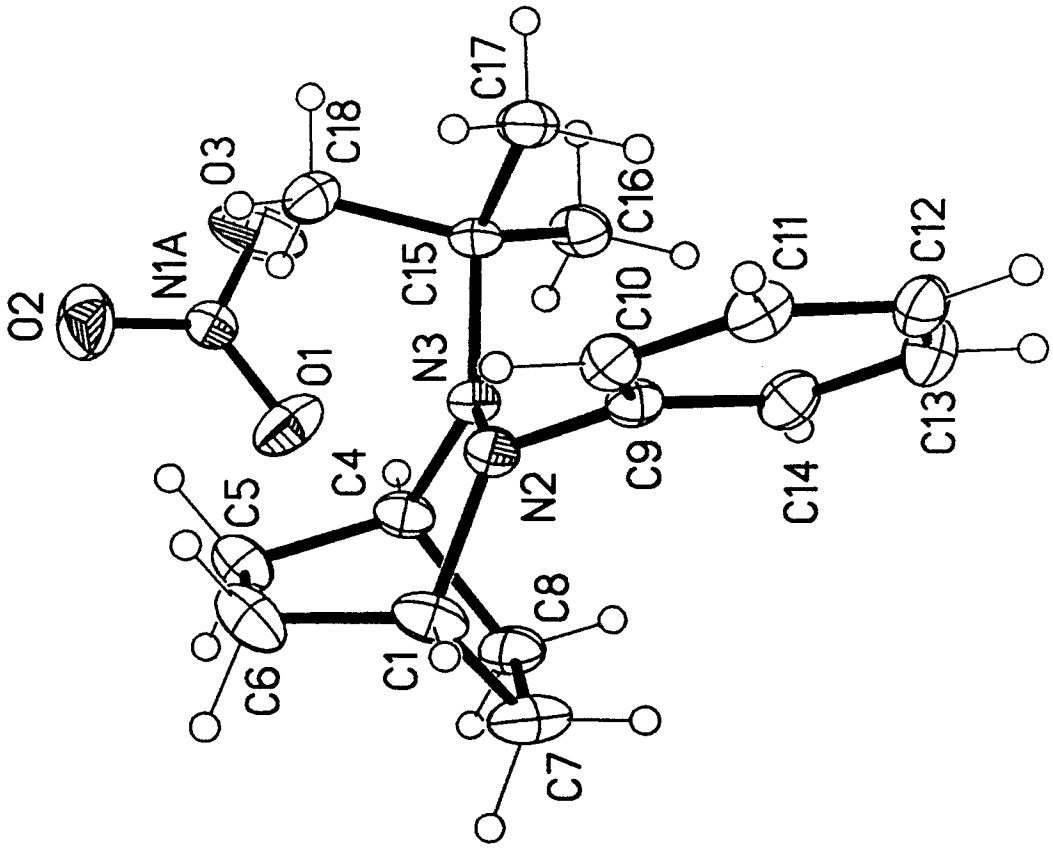
Table 8. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 2^+.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	24(2)	23(2)	22(2)	-3(1)	4(1)	0(1)
N(2)	19(1)	19(1)	19(1)	0(1)	1(1)	0(1)
N(3)	19(1)	21(1)	17(1)	-1(1)	1(1)	0(1)
C(4)	22(2)	26(2)	22(2)	-2(1)	-4(1)	-4(1)
C(5)	32(2)	24(2)	24(2)	-2(1)	0(1)	-6(1)
C(6)	30(2)	18(2)	26(2)	-3(1)	2(1)	-1(1)
C(7)	32(2)	29(2)	16(2)	-2(1)	2(1)	-5(1)
C(8)	30(2)	32(2)	23(2)	1(1)	-5(1)	-1(1)
C(9)	19(1)	21(2)	24(2)	0(1)	-2(1)	-2(1)
C(10)	30(2)	27(2)	40(2)	-9(1)	-1(2)	-3(1)
C(11)	51(2)	27(2)	32(2)	3(1)	-2(2)	-15(2)
C(12)	26(2)	34(2)	52(2)	-9(2)	-12(2)	4(1)
C(13)	22(2)	21(2)	17(2)	-1(1)	-1(1)	-1(1)
C(14)	22(2)	26(2)	20(2)	-1(1)	0(1)	1(1)
C(15)	22(2)	28(2)	20(2)	2(1)	-2(1)	3(1)
C(16)	24(2)	31(2)	18(2)	-3(1)	3(1)	-4(1)
C(17)	20(2)	42(2)	24(2)	-2(1)	2(1)	4(1)
C(18)	22(2)	37(2)	23(2)	3(1)	-3(1)	5(1)
C(19)	28(2)	76(3)	28(2)	0(2)	3(2)	-18(2)
N(20)	22(1)	43(2)	19(1)	2(1)	1(1)	-2(1)
N(21)	28(1)	28(1)	19(1)	3(1)	-1(1)	-1(1)
C(22)	48(2)	30(2)	28(2)	2(1)	10(2)	-8(2)
C(23)	79(3)	38(2)	43(2)	-6(2)	19(2)	-24(2)
C(24)	73(3)	77(3)	34(2)	-6(2)	9(2)	-49(2)
C(25)	29(2)	86(3)	33(2)	5(2)	8(2)	-22(2)
C(26)	53(2)	50(2)	29(2)	5(2)	11(2)	-18(2)
C(27)	27(2)	29(2)	20(2)	-1(1)	-1(1)	-2(1)
C(28)	35(2)	38(2)	28(2)	-4(1)	-1(1)	6(2)
C(29)	43(2)	38(2)	29(2)	-2(2)	-1(2)	-12(2)
C(30)	34(2)	51(2)	26(2)	2(2)	-5(1)	4(2)
B(1)	21(2)	23(2)	24(2)	0(1)	2(1)	-1(1)
C(1A)	24(2)	19(2)	20(2)	5(1)	2(1)	2(1)
C(2A)	26(2)	25(2)	28(2)	-1(1)	0(1)	2(1)
C(3A)	34(2)	28(2)	32(2)	-1(1)	9(2)	5(1)
C(4A)	51(2)	24(2)	22(2)	-5(1)	2(2)	3(2)
C(5A)	32(2)	24(2)	27(2)	2(1)	-7(1)	-3(1)
C(6A)	25(2)	22(2)	28(2)	-1(1)	0(1)	1(1)
C(1B)	23(2)	16(2)	25(2)	-3(1)	3(1)	-3(1)
C(2B)	26(2)	20(2)	26(2)	-2(1)	1(1)	-2(1)
C(3B)	22(2)	20(2)	39(2)	-1(1)	-7(1)	-1(1)
C(4B)	21(2)	28(2)	49(2)	-10(2)	2(2)	1(1)
C(5B)	31(2)	36(2)	33(2)	-15(2)	8(1)	-3(2)
C(6B)	29(2)	28(2)	28(2)	-4(1)	3(1)	-2(1)
C(1C)	20(2)	23(2)	28(2)	0(1)	-5(1)	7(1)
C(2C)	26(2)	28(2)	27(2)	4(1)	-4(1)	2(1)
C(3C)	27(2)	32(2)	39(2)	10(2)	1(1)	4(1)

C(4C)	21(2)	23(2)	54(2)	3(2)	-3(2)	1(1)
C(5C)	29(2)	37(2)	43(2)	-12(2)	-2(2)	-3(1)
C(6C)	29(2)	32(2)	34(2)	-6(1)	5(1)	-1(1)
C(1D)	38(2)	20(2)	22(2)	-6(1)	-1(1)	4(1)
C(2D)	45(2)	37(2)	27(2)	-5(2)	-4(2)	15(2)
C(3D)	68(3)	47(2)	27(2)	-7(2)	-13(2)	33(2)
C(4D)	97(3)	26(2)	19(2)	-2(1)	-4(2)	14(2)
C(5D)	81(3)	25(2)	23(2)	-3(1)	3(2)	-2(2)
C(6D)	53(2)	22(2)	22(2)	-4(1)	-2(2)	-2(2)



Thermal Ellipsoid Drawing (50% Probability Level) of the X-Ray Crystal Structure of $3^+ NO_3^-$.

Table 9. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 3^+.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	30(1)	26(1)	26(1)	-6(1)	-12(1)	4(1)
N(2)	20(1)	18(1)	18(1)	-3(1)	-1(1)	0(1)
N(3)	16(1)	18(1)	19(1)	-1(1)	-2(1)	1(1)
C(4)	21(1)	21(1)	25(1)	-2(1)	-4(1)	5(1)
C(5)	32(1)	28(1)	26(1)	6(1)	-5(1)	5(1)
C(6)	44(1)	36(1)	20(1)	-1(1)	-5(1)	10(1)
C(7)	22(1)	35(1)	48(1)	-5(1)	-12(1)	1(1)
C(8)	19(1)	32(1)	30(1)	-3(1)	-2(1)	6(1)
C(9)	17(1)	17(1)	22(1)	-2(1)	-2(1)	-2(1)
C(10)	21(1)	23(1)	18(1)	-4(1)	1(1)	-2(1)
C(11)	20(1)	18(1)	30(1)	-4(1)	1(1)	0(1)
C(12)	21(1)	23(1)	32(1)	6(1)	1(1)	-5(1)
C(13)	28(1)	31(1)	27(1)	2(1)	9(1)	-3(1)
C(14)	21(1)	25(1)	27(1)	-5(1)	5(1)	-1(1)
C(15)	15(1)	21(1)	19(1)	-2(1)	-4(1)	0(1)
C(16)	26(1)	34(1)	21(1)	-6(1)	-2(1)	1(1)
C(17)	20(1)	24(1)	28(1)	2(1)	-5(1)	0(1)
C(18)	20(1)	24(1)	32(1)	0(1)	1(1)	-2(1)
N(1A)	24(1)	18(1)	24(1)	-1(1)	-1(1)	4(1)
O(1)	25(1)	33(1)	63(1)	-1(1)	6(1)	-6(1)
O(2)	44(1)	59(1)	43(1)	15(1)	20(1)	18(1)
O(3)	64(1)	54(1)	52(1)	-20(1)	-35(1)	9(1)

Table 10. Bond lengths [Å] and angles [°] for 3^+.

C(1)-N(2)	1.491(2)	C(1)-C(6)	1.525(3)
C(1)-C(7)	1.533(3)	N(2)-N(3)	1.355(2)
N(2)-C(9)	1.440(2)	N(3)-C(4)	1.477(2)
N(3)-C(15)	1.522(2)	C(4)-C(5)	1.540(3)
C(4)-C(8)	1.540(3)	C(5)-C(6)	1.546(3)
C(7)-C(8)	1.545(3)	C(9)-C(14)	1.390(3)
C(9)-C(10)	1.399(2)	C(10)-C(11)	1.395(3)
C(11)-C(12)	1.391(3)	C(12)-C(13)	1.383(3)
C(13)-C(14)	1.396(3)	C(15)-C(17)	1.529(2)
C(15)-C(16)	1.529(3)	C(15)-C(18)	1.539(3)
N(1A)-O(3)	1.237(2)	N(1A)-O(2)	1.243(2)
N(1A)-O(1)	1.249(2)		

N(2)-C(1)-C(6)	107.8(2)	N(2)-C(1)-C(7)	107.2(2)
C(6)-C(1)-C(7)	111.9(2)	N(3)-N(2)-C(9)	120.77(13)
N(3)-N(2)-C(1)	113.05(14)	C(9)-N(2)-C(1)	117.03(14)
N(2)-N(3)-C(4)	113.02(14)	N(2)-N(3)-C(15)	123.69(13)
C(4)-N(3)-C(15)	120.55(13)	N(3)-C(4)-C(5)	110.5(2)
N(3)-C(4)-C(8)	106.71(14)	C(5)-C(4)-C(8)	109.5(2)
C(4)-C(5)-C(6)	108.1(2)	C(1)-C(6)-C(5)	108.6(2)
C(1)-C(7)-C(8)	108.4(2)	C(4)-C(8)-C(7)	108.4(2)
C(14)-C(9)-C(10)	121.6(2)	C(14)-C(9)-N(2)	121.0(2)
C(10)-C(9)-N(2)	117.3(2)	C(11)-C(10)-C(9)	118.5(2)
C(12)-C(11)-C(10)	120.4(2)	C(13)-C(12)-C(11)	120.0(2)
C(12)-C(13)-C(14)	120.9(2)	C(9)-C(14)-C(13)	118.5(2)
N(3)-C(15)-C(17)	113.16(14)	N(3)-C(15)-C(16)	107.27(14)
C(17)-C(15)-C(16)	111.2(2)	N(3)-C(15)-C(18)	107.12(14)
C(17)-C(15)-C(18)	107.3(2)	C(16)-C(15)-C(18)	110.8(2)
O(3)-N(1A)-O(2)	120.6(2)	O(3)-N(1A)-O(1)	119.4(2)
O(2)-N(1A)-O(1)	119.9(2)		

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 3^+.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	30(1)	26(1)	26(1)	-6(1)	-12(1)	4(1)
N(2)	20(1)	18(1)	18(1)	-3(1)	-1(1)	0(1)
N(3)	16(1)	18(1)	19(1)	-1(1)	-2(1)	1(1)
C(4)	21(1)	21(1)	25(1)	-2(1)	-4(1)	5(1)
C(5)	32(1)	28(1)	26(1)	6(1)	-5(1)	5(1)
C(6)	44(1)	36(1)	20(1)	-1(1)	-5(1)	10(1)
C(7)	22(1)	35(1)	48(1)	-5(1)	-12(1)	1(1)
C(8)	19(1)	32(1)	30(1)	-3(1)	-2(1)	6(1)
C(9)	17(1)	17(1)	22(1)	-2(1)	-2(1)	-2(1)
C(10)	21(1)	23(1)	18(1)	-4(1)	1(1)	-2(1)
C(11)	20(1)	18(1)	30(1)	-4(1)	1(1)	0(1)
C(12)	21(1)	23(1)	32(1)	6(1)	1(1)	-5(1)
C(13)	28(1)	31(1)	27(1)	2(1)	9(1)	-3(1)
C(14)	21(1)	25(1)	27(1)	-5(1)	5(1)	-1(1)
C(15)	15(1)	21(1)	19(1)	-2(1)	-4(1)	0(1)
C(16)	26(1)	34(1)	21(1)	-6(1)	-2(1)	1(1)
C(17)	20(1)	24(1)	28(1)	2(1)	-5(1)	0(1)
C(18)	20(1)	24(1)	32(1)	0(1)	1(1)	-2(1)
N(1A)	24(1)	18(1)	24(1)	-1(1)	-1(1)	4(1)
O(1)	25(1)	33(1)	63(1)	-1(1)	6(1)	-6(1)
O(2)	44(1)	59(1)	43(1)	15(1)	20(1)	18(1)
O(3)	64(1)	54(1)	52(1)	-20(1)	-35(1)	9(1)