Synthesis, Molecular Structure and Solution Dynamics of Dimeric Benzamidinates containing a Double Diazaallyl Lithium Bridge. A Rapid Interconversion of σ and π Bonds†

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Dimeric $Li[N(SiMe_3)_2]$ reacted with the nitriles $4\text{-}XC_6H_4CN$ (X = H or Me) in diethyl ether–hexane (1 : 10) to yield dimeric complexes $[4\text{-}XC_6H_4C(NSiMe_3)_2{\cdot}Li(NCC_6H_4X\text{-}4)]_2$ (X = H **1** or Me **2**). Complex **2** is dimeric in the solid state with two four-co-ordinated lithium cations bound in a *N,N'*-bidentate π fashion to one amidine anion (chelating), forming a double diazaallyl lithium bridge, in a monodentate σ fashion to a nitrogen lone pair of a substrate molecule, and monodentate to a nitrogen lone pair of a second amidine anion. In solution, rapid interconversion of the different lithium-amidine bonds (σ to π and *vice versa*) was observed by means of the NMR chemical shifts.

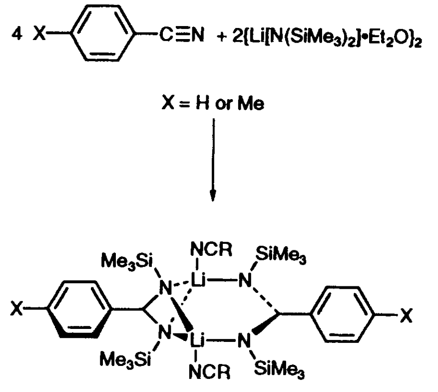
The chemistry of lithium is spreading within organic chemistry.[1] However, the co-ordination chemistry of organolithium compounds and the mechanisms of organolithium–base reactions are uncommonly complex and poorly understood.[2] This complexity stems from a high tendency of organolithium compounds to self-assemble into higher aggregates, which is considerably dependent on the choice of solvent and the precise preparation conditions. This complexity is enhanced also by the rapid solvent exchanges within the various aggregates as well as the extreme oxygen and moisture sensitivity of most organolithium derivatives. Thus, many organolithium reagents are prepared *in situ*, and there is no direct spectroscopic evidence of their solution- and solid-state structures.

N-Lithiated species constitute a very important class of organolithium reagents. They are the preferred bases for formation of ketone enolates,[3] generating low steady-state concentrations of some relatively unstable carbanions,[4] and for the preparation of heterocyclic thiazenes incorporating an RC(N–)N< moiety using lithium amidinates.[5] Recently,[6] main-group metallation of solvent-co-ordinated monomeric amidinates has been reported, giving a monomeric η^3-diazaallyl structure. Main group metallation of monoazaallyl[7a] and 2-aminopyridyl[7b] dimers has also been achieved. In the latter, the dimer is formed by one η^3-diazaallyl group and a σ bridge from the metal to the nitrogen lone pair of the second molecule. It should be pointed out that iminolithium compounds with N_2Li_2 moieties have been reported as in $(Bu^t{}_2C{=}NLi)_6$[8] although, in all the known structures, when both lithium metals are attached to the same two nitrogen atoms the latter atoms are not part of a η^3-diazaallyl arrangement.[2a]

In this paper we report the synthesis, low-temperature crystal structure and solution analysis of the first double lithium η^3-diazaallyl bridge in the *N,N'*-bis(trimethylsilyl)benzamidinate compounds: $[4\text{-}XC_6H_4C(NSiMe_3)_2{\cdot}Li(NCC_6H_4X\text{-}4)]_2$ (X = H **1** or Me **2**) and the rapid σ–π exchange of the bonding of the lithium atoms in solution.

Results and Discussion

Complexes **1** and **2** were first prepared by lithiating an equimolar solution of the corresponding benzonitrile with bis(trimethylsilyl)amido lithium dimer in diethyl ether–hexane (1 : 10) (Scheme 1). They are pale yellow, low-melting solids, highly soluble in organic solvents. By cooling a hexane solution of **2** at −40 °C a 30–40% crystallized product was obtained which was characterized by low-temperature X-ray diffraction and spectroscopic techniques. Higher yields (55–63% for **1** and **2**) can be obtained by using 2 : 1 mol ratios.



	R	X
1	H	H
2	C_6H_4Me-*p*	Me

Scheme 1

Crystal Structure of the Metallated Benzamidinate Dimer.—Suitable crystals of complex **2** were obtained from a hexane solution cooled slowly to −40 °C. Selected bond lengths and angles are listed in Table 1. The low-temperature X-ray analysis (Fig. 1) shows a dimeric benzamidinate structure with two, distorted-tetrahedral four-co-ordinated lithium cations each *N,N'*-chelated (π bond) by one bidentate benzamidinate moiety, singly co-ordinated (σ bond) to one nitrogen atom of a second benzamidinate, and attached (σ bond) to a nitrogen lone pair from an unreactive substrate molecule. The core units are two Li–N–C–N four-membered rings and a Li–N–C–N–Li–N six-membered ring. The two planes formed by the two η^3-diazaallyl systems make a dihedral angle of almost 90° thus forming a compound of distorted C_{2v} symmetry.‡ Within each amidinate moiety, **2**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ A compound of D_{2h} symmetry is theoretically expected, although a high-level computational comparison of both symmetries shows that C_{2v} is more stable than D_{2h} by 0.95 kcal mol^{-1} (*ca.* 3.97 kJ mol^{-1}).[9]

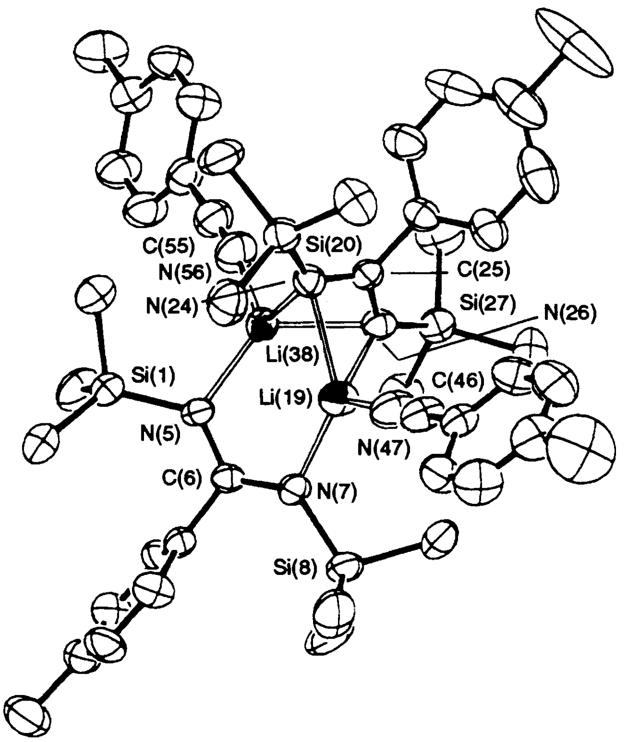


Fig. 1 Molecular structure of complex **2**

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Li(19)–N(7)	1.995(10)	Si(1)–N(5)	1.716(2)
Li(19)–N(24)	2.260(9)	N(5)–C(6)	1.340(5)
Li(19)–N(26)	2.108(10)	C(6)–N(7)	1.310(4)
Li(19)–N(47)	2.080(7)	N(7)–Si(8)	1.720(3)
Li(38)–N(5)	2.014(10)	Si(20)–N(24)	1.721(3)
Li(38)–N(24)	2.129(7)	N(24)–C(25)	1.320(5)
Li(38)–N(26)	2.161(7)	C(25)–N(26)	1.336(5)
Li(38)–N(56)	2.098(8)	N(26)–Si(27)	1.722(3)
N(7)–Li(19)–N(24)	138.8(5)	Si(8)–N(7)–Li(19)	117.2(3)
N(7)–Li(19)–N(26)	117.7(4)	Li(19)–N(24)–Si(20)	130.3(2)
N(7)–Li(19)–N(47)	115.1(3)	Li(19)–N(24)–C(25)	79.2(3)
N(24)–Li(19)–N(26)	62.9(2)	Li(19)–N(24)–Li(38)	68.0(3)
N(24)–Li(19)–N(47)	95.5(3)	Si(20)–N(24)–C(25)	131.8(3)
N(26)–Li(19)–N(47)	118.0(4)	Si(20)–N(24)–Li(38)	138.4(3)
N(5)–Li(38)–N(24)	117.7(3)	C(25)–N(24)–Li(38)	83.9(3)
N(5)–Li(38)–N(26)	125.8(4)	N(24)–C(25)–N(26)	118.5(3)
N(5)–Li(38)–N(56)	116.3(4)	Li(19)–N(26)–C(25)	84.9(3)
N(24)–Li(38)–N(26)	64.3(3)	Li(19)–N(26)–Si(27)	137.3(3)
N(24)–Li(38)–N(56)	118.2(3)	Li(19)–N(26)–Li(38)	70.3(3)
N(26)–Li(38)–N(56)	104.4(3)	C(25)–N(26)–Si(27)	131.4(2)
Si(1)–N(5)–C(6)	128.2(3)	C(25)–N(26)–Li(38)	82.3(3)
Si(1)–N(5)–Li(38)	111.2(3)	Si(27)–N(26)–Li(38)	127.5(3)
C(6)–N(5)–Li(38)	120.2(4)	Li(19)–N(47)–C(46)	178.0(5)
N(5)–C(6)–N(7)	123.6(3)	Li(38)–N(56)–C(55)	171.2(5)
C(6)–N(7)–Si(8)	130.7(2)	C(6)–N(7)–Li(19)	112.1(3)

shows C–N distances [N(5)–C(6) 1.340(5), C(6)–N(7) 1.310(4) Å and N(24)–C(25) 1.320(5), C(25)–N(26) 1.336(5) Å] which are almost the average of C=N [1.302(7)] and C–N [1.360(8) Å] bond lengths reported for similar protonated uncomplexed N-substituted phenyl ligands,[10] suggesting uniform delocalization throughout each three-atom centre unit. Hence, it seems that the anion in compound **2** is best described as a system containing two diazaallyl moieties, one of which acts as a double bridge of two lithiums. This description is sustained by the near planarity of the two major planes through the Si(20)–N(24)–C(25)–N(26)–Si(27) and Si(1)–N(5)–C(6)–N(7)–Si(8) units [Li(19)–N(7)–Si(8) 117.2, Li(19)–N(26)–Si(27) 137.3, Li(19)–N(24)–Si(20) 130.3, Li(38)–N(5)–Si(1) 111.2, Li(38)–N(24)–Si(20) 138.4, Li(38)–N(26)–Si(27) 127.5°]. The slight deviation from the plane can be rationalized by the electrostatic repulsion between the nitrogen atoms [N(5)···N(7) and N(24)···N(26)] sp^2 lone pairs, which is counterbalanced by the electrostatic attraction of the lithium cations for each of the nitrogen lone pairs.

Interestingly, two different bridge anion–lithium bond lengths exist for each metal atom [N(24)–Li(19) 2.260, N(26)–Li(19) 2.108 and N(24)–Li(38) 2.129, N(26)–Li(38) 2.161 Å]. The small difference in bond lengths for each lithium atom and the same nitrogen atom seems to be compensated by the corresponding elongation/contraction of the same lithium atom toward the corresponding substrate nitrogen lone pair to gain an even charge distribution around the lithium metal and around the heteroallylic nitrogen atoms.[9]

NMR Solution Behaviour of Metallated Benzamidinate Dimers.—The ^1H NMR (291 K, [$^2H_8$]toluene) spectra of compounds **1** and **2** show the characteristic resonance pattern for the N(SiMe$_3$) groups in accordance with the symmetric nature of the benzamidinate. In addition only one set of hydrogen resonances is observed for both amidine and the corresponding benzonitrile rings implying that in solution both aromatic rings have the same chemical environment. We were unable to discriminate between the different chemical shifts for the distinct trimethylsilyl and substituted arene groups even at low temperatures (173 K) suggesting, also by theoretical energy calculations,[9] that equivalent environments for the different groups are formed by rapid bond making [Li(19)–N(5) and Li(38)–N(7)] and breaking [Li(19)–N(24) and Li(38)–N(26)] σ to π and *vice versa*. The NMR solution studies were made in [$^2H_8$]tetrahydrofuran in order to avoid mixtures of the tetrahydrofuran (thf) solvated species.

Some transition metal/lanthanide and actinide complexes containing *N,N'*-bis(trimethylsilyl)benzamidinate have been reported in which the ligand exhibits a bidentate chelating mode.[11] For the transition metals the Li[N(SiMe$_3$)$_2$] was used with the nitrile as solvent, whereas in the lanthanide/actinide cases the lithium amidinates were used as precursors. Some investigations involving X-ray analysis of lithiated amidinates with strong chelating solvents such as hexamethylphosphoramide, which result in monomeric solvent-containing compounds, have been performed.[6] However, **2** is the first accurate crystal structure of an early main-group chelated cation with a doubly bridging diazaallyl unit, allowing comparison with the structures of known azaallyl-lithium and -sodium complexes.[7,12] Furthermore, a number of complexes which possess a [NR(C$_5$H$_4$N)]$^-$ (R = SiMe$_3$[7] or Ph[13]) anion chelating a lithium cation have been structurally characterized, although these are not strictly amidinates and do not have a fully delocalized diazaallyl unit as in **2**.

A comparison of compound **2** with lanthanide metal complexes of this benzamidinate reveals a small difference between the N(24)–C(25)–N(26) angle in **2** [118.5(3)] and in those in neodymium [121.4(5)[14]] and in ytterbium [119.8(2)[15]] complexes. This can be explained in terms of the slightly more ionic bonding character of the lanthanides. The opposite effect has been observed in a comparison of *N*-phenyl-substituted amidinates of late transition metals.[6a] It is very interesting to compare the Li–N–C–N planar core of **2** to similar four-membered cores in early main-group aza- and diaza-allyl complexes[7,14] and in the polymeric structure of benzyllithium[16] which clearly shows the change in bonding mode (from η^3 to σ,σ) of the lithium cation to the various allyl-type anions. In benzyllithium the cation is disposed asymmetrically above the allyl plane and located closest to the benzylic carbon. Allyllithium exists as an asymmetric π-bond structure as shown by NMR spectroscopy in thf which revealed a dimer.[17] For benzyl-potassium and -rubidium, the polymeric bonding involves η^3 and η^6 bridges.[18] For η^3-azaallyl complexes the

Table 2 Crystallographic data and structure refinement details for complex **2**

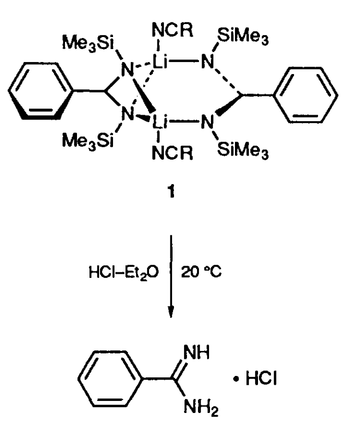
Formula	$C_{44}H_{64}Li_2N_6Si_4$
M	803.25
Crystal colour, shape	Yellow, prism
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size/mm	0.25 × 0.20 × 0.20
a/Å	13.571(7)
b/Å	13.967(7)
c/Å	15.131(8)
α/°	69.40(5)
β/°	74.10(5)
γ/°	83.56(5)
U/Å^3	2581.5
Z	2
F(000)	864
D_c/g cm^{-3}	1.033
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/mm^{-1}	0.14
Scan range (2θ)	4–50
Scan mode	ω–2θ
Scan width/°ω	1.2
Scan speed/°ω min^{-1}	3
No. measured reflections	8889
No. unique reflections	5117 $[F_o > 3\sigma(F_o)]$
No. refined parameters	763
Weighting scheme, w	$1.8161/[\sigma^2(F_o) + 0.000\,193F_o^2]$
R	0.074
R'	0.061
Minimum, maximum Δ/σ	−0.83, 1.12
Minimum, maximum residual electron density/e Å^{-3}	−0.34, 0.34

LiNCC system is not planar, being asymmetrically distorted toward the nitrogen; similarly the Na is located over the N above the CNC plane in the NaCNC core of the sodium azaallyl system. In **2** the core is also not planar, although each lithium atom is disposed symmetrically above and below the NCN core plane respectively. This non-planarity confirms the nature of the delocalized allyl π system which is involved in the bonding, rather than the sp^2 lone pair of each nitrogen which would require positioning of the lithium cation in the plane.

The lithium benzamidinate complexes react with acidic aqueous solutions yielding quantitatively the unsubstituted benzamidines (amidines are difficult to prepare by conventional routes and the reactions are of frequently low yield[19]) as in Scheme 2. The amidine in Scheme 2 was isolated almost quantitatively as the hydrochloride salt by precipitation.

Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr, *ca.* 1.33 × 10^{-3} Pa) line, or in a nitrogen-filled Vacuum Atmospheres glove-box with a medium-capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon from sodium–benzophenone. Hydrocarbon solvents ([$^2H_8$]toluene, C_6D_6, hexane) were distilled under nitrogen from Na–K alloy. All solvents for vacuum-line manipulations were stored *in vacuo* over Na–K alloy in resealable bulbs. Nitrile compounds (Aldrich) were degassed and freshly distilled under argon. The solid Li[N(SiMe$_3$)$_2$][20] was prepared according to the literature method. The ^{1}H NMR spectra were recorded on a Bruker AM 200 spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The experiments were conducted on Teflon valve-sealed tubes (J. Young) after vacuum transfer of the solvent in a high-vacuum line.



Scheme 2 R = Ph

Syntheses.—Complex **1**. To a magnetically stirred suspension of Li[N(SiMe$_3$)$_2$] (25.10 g, 0.15 mol) in dry diethyl ether (20 cm^3) was added (30.95 g, 0.30 mol) benzonitrile in dry hexane (200 cm^3). The homogeneous solution was stirred for 4 h and cooled to −60 °C. The precipitate was filtered off while cold yielding 36.6 g (63%) of complex **1**, m.p. = 56–58 °C (Found: C, 64.10; H, 7.40; N, 11.40. $C_{40}H_{56}Li_2N_6Si_4$ requires C, 64.35; H, 7.50; N, 11.25%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.19 (d, 4 H, J 7.7, *o*-H), 7.16 (d, 4 H, J 7.7, *o*-H), 6.95–6.89 (m, 8 H, *m*-H), 6.69 (t, 2 H, J 7.6, *p*-H), 6.50 (t, 2 H, J 7.7 Hz, *p*-H) and −0.03 (s, 36 H, SiMe).

Complex **2**. To a magnetically stirred suspension of Li[N(SiMe$_3$)$_2$] (25.10 g, 0.15 mol) in dry ether (20 cm^3) was added 35.15 g (0.30 mol) of toluonitrile in dry hexane (200 cm^3). The homogeneous solution was stirred for 4 h and cooled for a few hours at −78 °C. The precipitate was filtered off while cold yielding 33.12 g (55%) of complex **2**, m.p. 89–91 °C (Found: C, 65.95; H, 7.90; N, 10.70. $C_{44}H_{64}Li_2N_6Si_4$ requires C, 65.85; H, 8.00; N, 10.45%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.34 (d, 4 H, J 7.6), 7.04 (d, 4 H, J 8), 6.96 (d, 4 H, J 7.6), 6.48 (d, 4 H, J 8 Hz), 2.09 (s, Me, 6 H), 1.75 (s, Me, 6 H) and 0.212 (s, SiMe, 36 H).

Owing to the extreme sensitivity of this compound to moisture and oxygen, a suitable crystal for X-ray analysis was placed inside a glove-box in dry and degassed Parathon oil (Du-Pont). Then it was mounted on a Philips PW1100/20 four-circle diffractometer where it met a cold stream of nitrogen at 200 K. Reflections were collected and intensities were corrected in the usual way except for absorption. The structure was solved by direct methods,[21a] and refinement, based on F, was by block-diagonal least-squares.[21b] All non-hydrogen atoms were refined anisotropically in two blocks. Hydrogen atoms were included at calculated positions and refined isotropically in one block. The d(C–H) used was 1.08 Å. Preliminary data, measurement conditions and structure refinement are summarized in Table 2, final atomic coordinates in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Hydrolysis of Complex **1** *to Amidine Hydrochloride.*—To an ether solution containing complex **1** (8.03 g, 0.01 mol) at 0 °C were added 4 equivalents of 6 mol dm^{-3} HCl and the mixture stirred for 4 h. The precipitate was filtered through a C3 frit, washed with diethyl ether (3 × 20 cm^3) and recrystallized from ethanol–water to yield 2.65 g (85%) of benzamidine hydrochloride, m.p. 174–179 °C (lit.,[22] 166–168 °C).

Table 3 Atomic coordinates ($\times 10^4$) for complex **2**

Atom	*x*	*y*	*z*
Si(1)	2 099(1)	6 126(1)	316(1)
C(2)	1 781(4)	6 723(4)	1 289(4)
C(3)	2 661(4)	4 817(3)	791(4)
C(4)	814(4)	5 960(4)	145(4)
N(5)	2 803(2)	6 864(2)	−801(2)
C(6)	3 589(3)	7 470(3)	−996(3)
N(7)	3 935(3)	8 169(2)	−1 846(3)
Si(8)	5 006(1)	8 915(1)	−2 283(1)
C(9)	6 151(4)	8 317(5)	−1 808(5)
C(10)	4 702(5)	10 168(4)	−2 081(4)
C(11)	5 391(4)	9 204(4)	−3 618(4)
C(12)	4 064(3)	7 345(3)	−160(3)
C(13)	4 621(3)	6 461(3)	215(3)
C(14)	4 999(4)	6 320(3)	1 014(4)
C(15)	4 845(4)	7 037(4)	1 472(4)
C(16)	4 329(4)	7 934(4)	1 078(4)
C(17)	3 965(4)	8 090(3)	269(4)
C(18)	5 207(5)	6 854(4)	2 385(4)
Li(19)	3 041(6)	8 356(5)	−2 746(6)
Si(20)	341(1)	8 262(1)	−2 580(1)
C(21)	246(4)	8 964(4)	−1 716(4)
C(22)	27(4)	9 185(4)	−3 705(4)
C(23)	−633(4)	7 242(4)	−2 011(4)
N(24)	1 562(3)	7 745(3)	−2 730(3)
C(25)	2 196(4)	7 536(3)	−3 476(3)
N(26)	3 159(3)	7 253(2)	−3 429(3)
Si(27)	4 113(1)	6 711(1)	−4 129(1)
C(28)	4 803(4)	7 642(4)	−5 304(4)
C(29)	3 612(4)	5 664(4)	−4 390(4)
C(30)	5 062(4)	6 157(4)	−3 381(4)
C(31)	1 866(3)	7 652(3)	−4 386(3)
C(32)	2 251(4)	8 414(4)	−5 255(4)
C(33)	1 917(5)	8 543(5)	−6 079(4)
C(34)	1 185(6)	7 927(7)	−6 050(6)
C(35)	813(4)	7 152(6)	−5 204(6)
C(36)	1 142(4)	7 019(4)	−4 375(4)
C(37)	782(7)	8 116(7)	−6 952(6)
Li(38)	2 429(6)	6 596(5)	−1 892(5)
C(39)	2 341(3)	11 741(3)	−4 488(4)
C(40)	2 358(4)	12 505(4)	−4 116(4)
C(41)	2 196(4)	13 512(4)	−4 659(5)
C(42)	2 003(4)	13 756(4)	−5 555(5)
C(43)	1 976(4)	12 991(5)	−5 924(4)
C(44)	2 143(4)	11 981(4)	−5 383(4)
C(45)	1 870(7)	14 877(5)	−6 163(6)
C(46)	2 557(4)	10 698(4)	−3 944(4)
N(47)	2 749(3)	9 869(3)	−3 526(3)
C(48)	1 966(4)	3 109(4)	−1 155(4)
C(49)	2 460(4)	2 455(4)	−492(4)
C(50)	2 345(4)	1 410(4)	−220(4)
C(51)	1 745(4)	1 008(3)	−606(4)
C(52)	1 255(4)	1 672(4)	−1 267(4)
C(53)	1 359(4)	2 727(4)	−1 560(4)
C(54)	1 611(4)	−133(4)	−294(4)
C(55)	2 095(4)	4 205(4)	−1 454(4)
N(56)	2 205(3)	5 062(3)	−1 685(3)

Acknowledgements

This research was supported by the fund for the promotion of research at the Technion and the Argentinian Research Fund.

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Received 14*th June* 1994; *Paper* 4/03582H