Effect of *N*-Aryl Substituents on the Reactivity of Electron-rich Olefins as Precursors of Transition-metal–Carbene Complexes. The Crystal and Molecular Structure of *NN'N''N'''*-Tetraphenylbis(1,3-imidazolidin-2-ylidene), and its π-Electron Distribution

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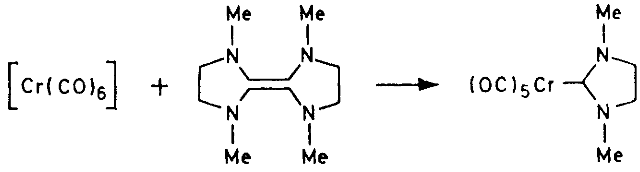
The title compound (L^{Ph}_2) crystallises in space group $P2_1/c$ with a = 10.854(8), b = 13.258(8), c = 8.225(6) Å, β = 98.19(5)°, and Z = 2, and the structure has been refined to R = 0.050 based on 1 233 counter reflections. The molecule has a non-planar geometry of approximate C_{2h} point-group symmetry which minimises steric strain between vicinal phenyl rings. The π-electron distribution in the molecule as calculated by Hückel theory shows that, relative to an *N*-methyl-substituted electron-rich olefin (L^{Me}_2) of similar geometry, the phenyl groups in L^{Ph}_2 have increased the positive π-electron charge on the nitrogen atoms. This supports the view that the reduced reactivity of L^{Ph}_2 relative to L^{Me}_2 in reactions with transition-metal complexes to form carbene complexes is due to inhibition of an initial rate-determining step of attack by the metal at one of the nitrogen atoms of the electron-rich olefin.

ELECTRON-RICH olefins of the type where the C=C double bond has four amino-substituents show much enhanced reactivity towards electrophilic attack,[1-3] particularly cycloaddition at, and in some cases cleavage of, the double bond, and also ready oxidation to a mono- or di-cation. Recent papers by Lappert and his co-workers[4,5] have shown that the cyclic electron-rich olefins of the type (1), abbreviated as L^R_2, where R = n-alkyl, benzyl, or phenyl, are also effective precursors of transition-metal carbene complexes.



(1) R = Me

In this paper I investigate the causes of the reduced reactivity of the *N*-aryl-substituted electron-rich olefins, *e.g.* L^{Ph}_2, compared to the *N*-alkyl-substituted olefin L^{Me}_2 in reactions of this type. The proposed mechanism of the reaction [5] invoked initial co-ordination of the olefin to the metal by one nitrogen atom followed by rearrangement to a C(olefin)-bonded species and fragmentation to form the carbene–metal complex. Previously suggested causes for the decreased reactivity of L^{Ph}_2 have been the decrease in the relative energy of the highest occupied orbital (h.o.m.o.),[2] or the increase in the positive charge on the nitrogen atoms [6] due to the interaction with the π electrons of the phenyl rings. Both ideas implicitly assume an extended planar molecule with the trigonal-planar nitrogen atoms coplanar with the phenyl rings, whilst, as has previously been pointed out,[5] the steric strain between vicinal phenyl groups must result in a non-planar molecule probably of either C_{2h} or D_2 point-group symmetry. The crystal structure of the title compound L^{Ph}_2 has now been determined, and the approximate π-electron distributions calculated for possible conformations to see whether the reduction in reactivity is associated with the effects of the π electrons of the phenyl rings or simply with the non-planarity of the molecule.

RESULTS

Crystal Structure of L^{Ph}_2.—The molecular conformation and atom numbering scheme of L^{Ph}_2 are shown in Figure 1 in a view perpendicular to the mean plane of the olefin. The numbering of the hydrogen atoms follows that of the carbon atom to which they are attached. Final atomic co-ordinates are in Table 1, bond lengths, bond angles, and torsion angles in Table 2. The molecule has a crystallographically imposed inversion centre and overall idealised C_{2h} point-group symmetry. A study of the various mean-plane calculations (Table 3) and the side view of the molecule (Figure 2) reveals that the observed conformation of

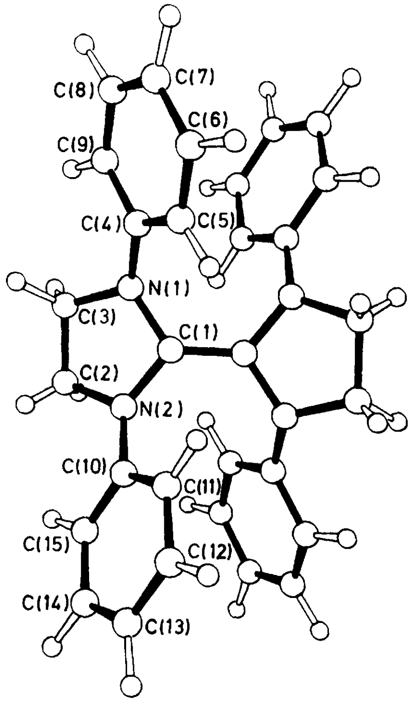


FIGURE 1 Molecular stereochemistry and atom-numbering scheme of L^{Ph}_2 viewed perpendicular to the mean plane of the olefin

the molecule involves only a small tetrahedral distortion at the nitrogen and olefin carbon atoms, and is caused mainly by a rotation about the N–C(olefin) bonds to bring the ring and phenyl C atoms on opposite sides of the olefinic mean plane by equivalent amounts for all four N atoms, plus a rotation about each N–C(phenyl) bond equally for all four N atoms. Thus the C_2H_4 fragment (plane A) is roughly planar as are the NC_3 fragments (planes B and C) and the phenyl rings (planes D and E). However, they are each non-coplanar with respect to each other, the angles averaging 40° from A to B and A to C, and 26° from B to D and D to E. This is consistent with a tendency to maintain the π-bonding system extending over the olefin and nitrogen atoms out to the phenyl rings. The observed distortion effectively moves the vicinal phenyl rings apart to an almost parallel arrangement with minimum contact distances of

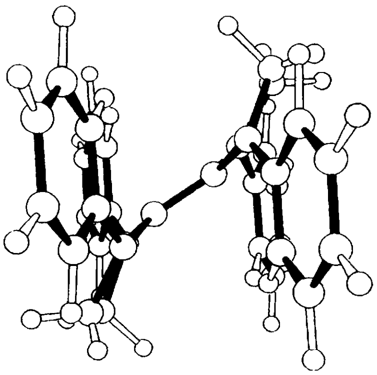


FIGURE 2 L^{Ph}_2 viewed parallel to the mean plane of the olefin

TABLE 1

Final atomic co-ordinates (× 10^4) of L^{Ph}_2 with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
N(1)	−687(2)	1 212(2)	−0 900(3)
N(2)	1 184(2)	1 006(2)	663(3)
C(1)	83(2)	513(2)	036(3)
C(2)	1 341(3)	1 861(2)	−398(4)
C(3)	48(3)	2 063(3)	−1 250(4)
C(4)	−1 960(3)	1 307(2)	−845(3)
C(5)	−2 532(3)	824(2)	350(3)
C(6)	−3 801(3)	0 911(2)	333(4)
C(7)	−4 516(3)	1 465(2)	−846(4)
C(8)	−3 959(3)	1 956(3)	−2 008(4)
C(9)	−2 691(3)	1 881(2)	−2 027(4)
C(10)	1 844(2)	880(2)	2 221(3)
C(11)	1 316(3)	381(2)	3 442(3)
C(12)	2 010(3)	231(3)	4 961(4)
C(13)	3 215(3)	581(3)	5 300(4)
C(14)	3 728(3)	1 091(3)	4 102(4)
C(15)	3 056(3)	1 238(2)	2 574(4)
H(2A)	1 710	2 362	186
H(2B)	1 949	1 626	−1 351
H(3A)	40	2 252	−2 133
H(3B)	−371	2 786	−957
H(5)	−2 065	0 381	1 280
H(6)	−4 200	465	1 187
H(7)	−5 504	1 446	−955
H(8)	−4 479	2 428	−2 828
H(9)	−2 213	2 310	−2 776
H(11)	389	145	3 260
H(12)	1 579	−149	5 894
H(13)	3 764	433	6 439
H(14)	4 671	1 398	4 383
H(15)	3 464	1 689	1 624

TABLE 2

Bond lengths and angles with estimated standard deviations in parentheses and selected torsion angles

(*a*) Bonds (Å)

C(1)–C(1)′	1.372(6)	C(6)–C(7)	1.367(4)
C(1)–N(1)	1.403(3)	C(7)–C(8)	1.367(5)
C(1)–N(2)	1.395(3)	C(8)–C(9)	1.381(5)
N(1)–C(3)	1.434(4)	C(9)–C(4)	1.391(4)
N(2)–C(2)	1.455(4)	C(10)–C(11)	1.392(4)
C(2)–C(3)	1.501(4)	C(11)–C(12)	1.378(4)
N(1)–C(4)	1.395(4)	C(12)–C(13)	1.378(5)
N(2)–C(10)	1.386(3)	C(13)–C(14)	1.377(5)
C(4)–C(5)	1.391(4)	C(14)–C(15)	1.374(4)
C(5)–C(6)	1.381(4)	C(15)–C(10)	1.389(4)
C(2)–H(2A)	0.88	C(8)–H(8)	1.03
C(2)–H(2B)	1.14	C(9)–H(9)	1.03
C(3)–H(3A)	0.77	C(11)–H(11)	1.04
C(3)–H(3B)	1.10	C(12)–H(12)	1.08
C(5)–H(5)	1.04	C(13)–H(13)	1.06
C(6)–H(6)	1.06	C(14)–H(14)	1.10
C(7)–H(7)	1.07	C(15)–H(15)	1.12

(*b*) Angles (°)

C(1′)–C(1)–N(1)	124.5(4)	C(4)–C(5)–C(6)	119.9(3)
C(1′)–C(1)–N(2)	125.5(4)	C(5)–C(6)–C(7)	121.1(3)
N(1)–C(1)–N(2)	107.8(2)	C(6)–C(7)–C(8)	119.3(3)
C(1)–N(1)–C(13)	109.0(2)	C(7)–C(8)–C(9)	121.0(3)
C(1)–N(1)–C(4)	123.9(2)	C(8)–C(9)–C(4)	120.1(3)
C(3)–N(1)–C(4)	121.2(2)	N(2)–C(10)–C(11)	120.8(2)
C(1)–N(2)–C(2)	108.1(2)	N(2)–C(10)–C(15)	120.1(3)
C(1)–N(2)–C(10)	126.0(2)	C(11)–C(10)–C(15)	119.1(2)
C(2)–N(2)–C(10)	124.0(2)	C(10)–C(11)–C(12)	119.6(3)
N(2)–C(2)–C(3)	103.7(2)	C(11)–C(12)–C(13)	121.0(3)
C(2)–C(3)–N(1)	106.0(3)	C(12)–C(13)–C(14)	119.3(3)
N(1)–C(4)–C(5)	121.6(2)	C(13)–C(14)–C(15)	120.5(3)
N(1)–C(4)–C(9)	119.8(3)	C(14)–C(15)–C(10)	120.4(3)
C(5)–C(4)–C(9)	118.6(3)		

(*c*) Torsion angles (°)

N(2′)–C(1′)–C(1)–N(1)	−18.8
N(1′)–C(1′)–C(1)–N(2)	18.8
C(1′)–C(1)–N(2)–C(2)	139.9
C(1′)–C(1)–N(1)–C(3)	−147.9
C(1′)–C(1)–N(1)–C(4)	59.2
C(1′)–C(1)–N(2)–C(10)	−55.4
C(1)–N(1)–C(4)–C(5)	10.8
C(1)–N(2)–C(10)–C(11)	−13.2
C(1)–N(2)–C(2)–C(3)	21.7
C(1)–N(1)–C(3)–C(2)	−2.2
C(4)–N(1)–C(3)–C(2)	151.6
C(10)–N(2)–C(2)–C(3)	−143.3
N(2)–C(2)–C(3)–N(1)	−11.7
C(3)–N(1)–C(4)–C(5)	−138.9
C(2)–N(2)–C(10)–C(11)	149.2

TABLE 3

Deviations (Å) of atoms from various mean planes. Atoms not included in the calculation of the plane are marked with a superscript dagger

Plane A: C(1) 0.00, C(1′) 0.00, D(1) 0.00,* D(1′) 0.00, N(1) † −0.19, N(2) † −0.19

Plane B: C(1) 0.00, C(3) 0.00, C(4) 0.00, N(1) † −0.20

Plane C: C(1) 0.00, C(2) 0.00, C(10) 0.00, N(2) † −0.11

Plane D: C(4) −0.01, C(5) 0.00, C(6) 0.00, C(7) −0.01, C(8) 0.01, C(9) 0.00, N(1) † −0.05

Plane E: C(10) −0.01, C(11) 0.01, C(12) 0.00, C(13) −0.01, C(14) 0.01, C(15) 0.00, N(2) † −0.05

Plane F: N(1) −0.04, N(2) 0.04, C(2) −0.07, C(3) 0.07, C(1) † −0.28

Angles (°) between planes: A–B 38, A–C 41, A–D 61, A–E 60, A–F 33, B–C 44, B–D 28, B–E 45, B–F 20, C–D 45, C–E 23, C–F 23, D–E 31, D–F 30, E–F 30

* C(1′) is related to C(1) by the inversion $\bar{x},\bar{y},\bar{z}$. D(1) is the midpoint of the line joining N(1) and N(2′).

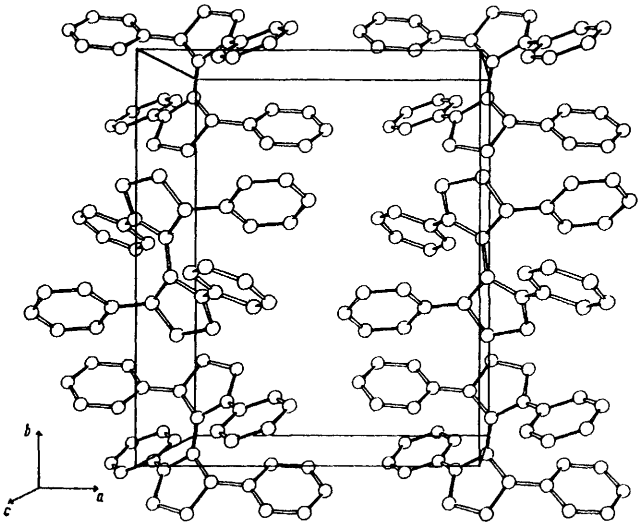


FIGURE 3 Crystal packing of $L^{Ph}{}_2$

3.1 Å for C · · · C and 2.8 Å for C · · · H (Table 4). The imidazoline rings have an envelope conformation with the N–C–N moieties as the flap. The phenyl rings are planar and show reduced internal angles (mean 118.9°) at the C atoms bonded to nitrogen, as seen elsewhere [7] in phenyl rings with electronegative substituents. The averaged bond lengths around the phenyl rings show that the two C–C bonds adjacent to the N atom (mean 1.39 Å) are slightly longer than the remaining bonds (mean 1.376 Å). Both of the *ortho*-hydrogen atoms of each phenyl ring are involved in close H · · · H and H · · · C contacts with the other phenyl rings and the methylene groups of the imidazoline rings, *e.g.* H(5) · · · H(11) 2.9 Å and H(15) · · · C(2) 2.7 Å (Table 4). The crystal packing of the structure is shown in Figure 3 and calculations of intermolecular contacts reveal none significantly shorter than the sum of the relevant van der Waals radii.

π-Electron Distribution.—Simple Hückel theory was used to calculate π-electron distributions for hypothetical conformations of $L^{Ph}{}_2$ and $L^{Me}{}_2$. Whilst obviously open to criticism in terms of the absolute value of the results, these calculations might be expected to give some idea of the differences in π-electron properties of closely related molecules. The results are summarised in Table 5. The relative energy of the h.o.m.o. is seen to be virtually insensitive to the presence of the phenyl rings but significantly reduced in energy in $L^{Ph}{}_2$ by the non-polar conformation imposed by the steric constraints. The negative π-electron charge on the olefinic C atoms is only slightly reduced in $L^{Ph}{}_2$ and is affected almost equally by the non-planar distortion and the presence of the phenyl rings. On the other hand, the positive π-electron charge on the N atoms is significantly increased in $L^{Ph}{}_2$, being affected almost entirely by the presence of the phenyl rings and not by the non-planar distortion.

TABLE 4

Short intramolecular non-bonded contacts (Å). Atoms in the other half of the molecule related by the inversion centre are indicated by primes

N(1) · · · C(10′)	3.17	C(1) · · · H(11′)	2.80
N(1) · · · C(11′)	2.98	C(4) · · · C(10′)	3.12
N(1) · · · H(11′)	2.70	C(4) · · · C(11′)	3.24
N(2) · · · C(4′)	3.18	C(4) · · · H(11′)	3.39
N(2) · · · C(5′)	3.01	C(5) · · · C(10′)	3.25
N(2) · · · H(5′)	2.70	H(2B) · · · H(5′)	2.66
C(1) · · · H(5′)	2.80	H(3A) · · · H(11′)	3.32
H(9) · · · C(3)	2.61	H(15) · · · C(2)	2.65
H(9) · · · H(3A)	2.42	H(15) · · · H(2A)	2.28
H(9) · · · H(3B)	2.40	H(15) · · · H(2B)	2.75
H(5) · · · H(11)	2.93		

The results of the calculation for the observed geometry of $L^{Ph}{}_2$ are compared in Figure 4 with the observed bond lengths and reflect qualitatively the trends in relative bond lengths for bonds of the same type.

TABLE 5

Hückel molecular-orbital calculations * using $\alpha_N = \alpha + 1.5\beta$ and $\beta_{C-N} = \beta \cos \phi$ where ϕ is the angle of rotation away from coplanarity

		π-electron charge		Relative energy of
Molecule	Geometry	C(olefin)	N	h.o.m.o.
$L^{Me}{}_2$	Hypothetical planar skeleton	−0.17	+0.08	$\alpha - 0.19\beta$
$L^{Ph}{}_2$	Hypothetical planar skeleton	−0.13	+0.22	$\alpha - 0.14\beta$
$L^{Me}{}_2$	Distorted from planar geometry as for $L^{Ph}{}_2$,*i.e.* rotations of 40° about the N–C(olefin) bonds	−0.12	+0.06	$\alpha + 0.14\beta$
$L^{Ph}{}_2$	Distorted from planar geometry as in the observed conformation, *i.e.* rotations of 40° about the N–C(olefin) bonds, and 26° about the N–C(phenyl) bonds	−0.11	+0.18	$\alpha + 0.11\beta$

* A. Streitweiser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

DISCUSSION

The *N*-phenyl-substituted electron-rich olefin $L^{Ph}{}_2$ has been shown to have a non-planar geometry in which π-electron delocalisation is not as high as in a hypothetical all-planar conformation. However, it is also known [8] that an *N*-benzyl-substituted electron-rich olefin has a geometry which is equally as non-planar although of D_2 not C_{2h} symmetry, and we must therefore look for the causes of the reduced reactivity of $L^{Ph}{}_2$ relative to $L^{Me}{}_2$ in those effects that are caused specifically by the phenyl rings and not in those due to the non-planarity

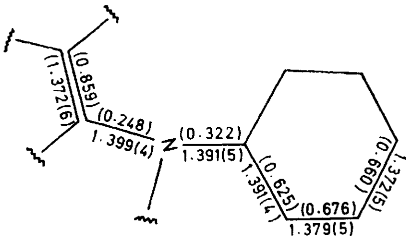


FIGURE 4 A comparison of π-bond orders, in parentheses, calculated for the observed geometry, and the observed bond lengths (Å) averaged over chemically equivalent bands. The estimated standard deviations quoted are either the largest of those of the individual bonds or the root-mean-square deviations, whichever is larger

alone. For this reason it seems that the most probable cause is the increased positive π-electron charge on the nitrogen atoms of $L^{Ph}{}_2$. This fits in nicely with the proposed mechanism of reaction with transition-metal complexes if one assumes that the rate-controlling step is the initial co-ordination of one nitrogen atom of the olefin to the metal. This would be much less likely where there is increased positive charge on the nitrogen atoms.

It is, of course, also possible that the difference in reactivity is due to steric blocking of attack on the olefin and indeed the molecular structure of $L^{Ph}{}_2$ shows that four of the *ortho*-hydrogen atoms of the phenyl rings lie either side of the centre of the C=C bond above and below it at a distance of 2.8 Å. This might well cause steric blocking of access by an incoming electrophile directly at the olefinic C atoms, but less so if initial attack is at the nitrogen atom. There is also the possibility that the blocking effect slows down the second step of the proposed mechanism where the metal transfers from the nitrogen to an olefinic carbon atom.

Some evidence on the relative importance of electronic and steric effects comes from a comparison of the reactivities of the related electron-rich olefins with *p*-tolyl, *p*-anisyl, and *o*-anisyl substituents.[9] The observed order of reactivity of $L^{R}{}_2$ in comparable reactions with metal complexes is *p*-anisyl > *p*-tolyl > Ph > *o*-anisyl, which for the first two is consistent with the cause being the electron-releasing effects of the *para* substituents in decreasing the positive charge on the nitrogen atoms, and inconsistent with steric blocking since both these olefins would be expected to have comparable conformations to $L^{Ph}{}_2$. On the other hand, the much reduced reactivity of the electron-rich *o*-anisyl olefin can be rationalised by the observation of the several very short intramolecular contacts of *ortho*-hydrogen atoms of each phenyl ring in $L^{Ph}{}_2$ in both of the two different positions exemplified by H(5) and H(9). In either position replacement of the H atom by a methoxy-group would produce implausibly short contacts with the rest of the molecule and it seems probable that the geometry of *o*-anisyl olefin is substantially more non-planar than $L^{Ph}{}_2$, possibly by adoption of the alternative D_2-type distortion seen [8] in the structure of $L^{CH_2Ph}{}_2$ where additional steric strain can be taken up by further rotation about the C=C double bond. Other electron-rich *N*-aryl olefins with *ortho* substituents on the aryl group would also be expected to show decreased reactivity relative to $L^{Ph}{}_2$, for the same reason.

EXPERIMENTAL

A crystalline sample of the title compound was kindly provided by Dr. P. L. Pye.

Crystal Data.—$C_{30}H_{28}N_4$, $M = 444.6$, Monoclinic, $a = 10.854(8)$, $b = 13.258(8)$, $c = 8.225(6)$ Å, $\beta = 98.19(5)°$, $U = 1\,171.5$ Å^3, $Z = 2$, $D_c = 1.26$ g cm^{-3}, $F(000) = 472$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 0.4$ cm^{-1}, space group $P2_1/c$ from systematic absences $0k0$ for k odd and $h0l$ for l odd.

A crystal of size 0.3 × 0.3 × 0.1 mm, mounted along the main-face diagonal parallel to the '*b*' axis, was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were derived from setting angles for 12 reflections. Intensities of reflections in the quadrant $hk \pm l$ with $2 < \theta < 25°$ were measured using an ω—2θ step scan with Mo-K_α radiation and a graphite-crystal monochromator. Reflections were scanned in 60 steps of 0.5 s and 0.01°, each with background counts of 15 s at each end of the scan. Three standard reflections remeasured after every 100 reflections showed no significant change during the data collection. After correction for Lorentz and polarisation effects but not for absorption and after averaging of any symmetry-equivalent data, 1 233 reflections with $I > 3\sigma(I)$ based on counting statistics were used in the structure analysis.

With $Z = 2$ in space group $P2_1/c$ the molecule must lie across a crystallographic inversion centre and application of the direct-method routines of SHELX revealed all non-hydrogen atoms of such a molecule. Full-matrix least-squares refinement of positions and anisotropic thermal parameters reduced R to 0.090 and a difference synthesis revealed the positions of all the hydrogen atoms. Hydrogen atoms attached to the phenyl rings were better defined and had more reasonable C–H bond lengths (mean 1.06 Å) than the methylene hydrogen atoms (mean C–H 0.97 Å). Continued refinement with H atoms included at fixed positions, with isotropic thermal parameters equal to those of the C atom to which they were attached, converged at $R = 0.050$, $R' = 0.072$, with a maximum shift-to-error of 0.08. The weighting scheme was $w = 0.95/[\sigma^2(F) + 0.003\,2F^2]$. A final difference map was everywhere < 0.2e Å^{-3}.

Initial data processing was done with local programs and the structure solution and refinement was carried out with the SHELX program system of G. M. Sheldrick. Scattering factors for neutral atoms and dispersion corrections were taken from ref. 10. Lists of thermal parameters and final structure factors have been deposited as Supplementary Publication No. SUP 22525 (10 pp.).[*]

[8/1272 *Received*, 10*th July*, 1978]

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.