Purification and *X*-Ray Crystal Structure of Bis[tris(trimethylsilyl)methyl]diarsene†

Alan H. Cowley,* Nicholas C. Norman, and Marek Pakulski
Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, U.S.A.

The crystal and molecular structure of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ has been determined by *X*-ray diffraction. The diarsene crystallizes in space group $P\bar{1}$ (no. 2), with $a = 9.151(3)$, $b = 12.682(2)$, $c = 15.537(4)$ Å, $\alpha = 70.07(2)$, $\beta = 89.61(2)$, $\gamma = 87.88(2)°$, and $Z = 2$. The compound is isostructural with $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ and adopts a *trans*-planar conformation with As=As = 2.245(1), 2.243(1) Å and As–As–C = 106.2(2), 106.4(2)° in two crystallographically independent molecules. Trends in the structures of RE=E′R′[E=E′=N or P, R=R′=$C_6H_2Bu^t_3$-2,4,6; E=E′=P, R=R′=$C(SiMe_3)_3$ or $NBu^t(SiMe_3)$; E=E′=As, R=R′=$C(SiMe_3)_3$ or R=$C_6H_2Bu^t_3$-2,4,6,R′=CH-$(SiMe_3)_2$; E=P,E′=As, R=$C_6H_2Bu^t_3$-2,4,6,R′=$CH(SiMe_3)_2$] are discussed.

The use of bulky groups has permitted the isolation of an increasing number of double-bonded molecules featuring heavier Group 4B and 5B elements.[1] In Group 5B, most of the effort has been directed towards the synthesis and characterisation of diphosphenes (RP=PR′). At the present time, only two diarsenes have been reported, $(2,4,6\text{-}Bu^t_3C_6H_2)As{=}AsCH(SiMe_3)_2$ (**1**)[2] and $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**).[3] Whilst the *X*-ray crystal structure of (**1**) provided the first experimental measurement of the length of an unsupported arsenic–arsenic double bond, we realised that the structure of (**2**) would, in fact, be more interesting because it would afford the first comparison of a diphosphene and a diarsene with the same ligand set. Initial efforts to purify and crystallise (**2**) were frustrated by the facile decomposition of this compound. These difficulties have now been surmounted, and the newly available metric parameters permit a more extensive discussion of the structural trends for RE=E′R′ molecules.

Results and Discussion

The diarsene (**2**) was prepared by the procedure of Couret *et al.*,[3] involving the reaction of $AsCl_2[C(SiMe_3)_3]$ with $LiBu^t$. Careful purification of (**2**) was necessary in order to obtain crystals suitable for *X*-ray crystallography. Full details are given in the Experimental section.

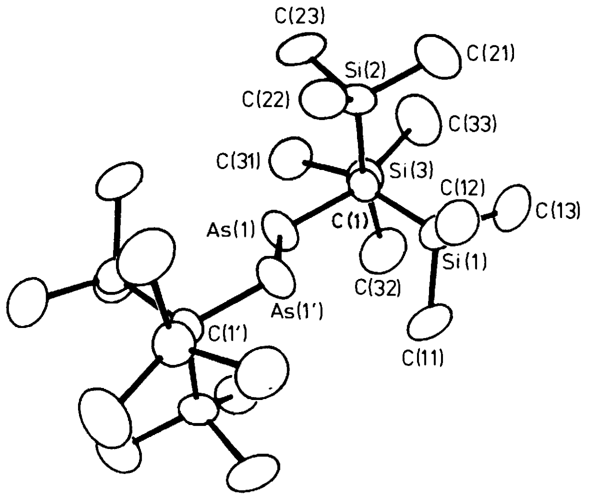


Figure 1. ORTEP view of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**), molecule A

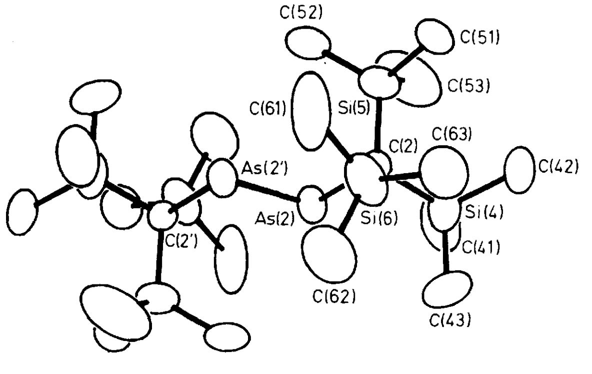


Figure 2. ORTEP view of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**), molecule B

Compound (**2**) crystallises in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit. As in the case of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$,[4] two crystallographically independent half-molecules are present in the asymmetric unit, each being related to the other by a centre of inversion. The two crystallographically independent molecules are illustrated in Figures 1 and 2, together with the atom-numbering scheme. Tables of bond lengths, bond angles, and atomic positional parameters are presented in Tables 1—3, respectively. The arsenic–arsenic bond lengths [2.245(1) and 2.243(1) Å] and As–As–C angles [106.2(2) and 106.4(2)°] for molecules A and B of (**2**) are the same within experimental error. Both molecules adopt a *trans* geometry, and the C–As–As–C atoms are crystallographically planar. Moreover, the conformations of molecules A and B are very similar, as indicated by the various torsion angles. For example, for molecule A As(1′)–As(1)–C(1)–Si(1) = 43.6, As(1′)–As(1)–C(1)–Si(2) = −80.0, and As(1′)–As(1)–C(1)–Si(3) = 163.6°, whilst for molecule B As(2′)–As(2)–C(2)–Si(6) = 48.8, As(2′)–As(2)–C(2)–Si(5) = −75.2, and As(2′)–As(2)–C(2)–Si(4) = 166.3°.

The average As–As bond length [2.244(1) Å] is slightly larger than that for (**1**) [2.224(2) Å].[2] However, both values are close to the sum of the double bond covalent radii for As (2.22 Å).[5] Furthermore, the As–As bond lengths for (**1**) and (**2**) are appreciably shorter than the range (2.43—2.46 Å) which has

---

† *Supplementary data available* (No. SUP 56082, 5 pp.): H-atom co-ordinates, thermal parameters, torsion angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Bond lengths (Å) for $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**) with estimated standard deviations in parentheses

Molecule A		Molecule B	
As(1)–As(1′)	2.245(1)	As(2)–As(2′)	2.243(1)
As(1)–C(1)	2.000(6)	As(2)–C(2)	2.002(6)
Si(1)–C(1)	1.889(6)	Si(4)–C(2)	1.905(6)
Si(1)–C(11)	1.909(8)	Si(4)–C(41)	1.886(10)
Si(1)–C(12)	1.918(8)	Si(4)–C(42)	1.894(8)
Si(1)–C(13)	1.900(8)	Si(4)–C(43)	1.947(11)
Si(2)–C(1)	1.927(7)	Si(5)–C(2)	1.886(7)
Si(2)–C(21)	1.876(8)	Si(5)–C(51)	1.867(8)
Si(2)–C(22)	1.890(7)	Si(5)–C(52)	1.841(9)
Si(2)–C(23)	1.891(8)	Si(5)–C(53)	1.933(12)
Si(3)–C(1)	1.932(6)	Si(6)–C(2)	1.907(6)
Si(3)–C(31)	1.884(8)	Si(6)–C(61)	1.946(10)
Si(3)–C(32)	1.899(9)	Si(6)–C(62)	1.810(10)
Si(3)–C(33)	1.891(8)	Si(6)–C(63)	1.897(8)

Table 2. Bond angles (°) for $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**) with estimated standard deviations in parentheses

Molecule A		Molecule B	
As(1′)–As(1)–C(1)	106.2(2)	As(2′)–As(2)–C(2)	106.4(2)
C(1)–Si(1)–C(11)	113.2(3)	C(2)–Si(4)–C(41)	116.4(4)
C(1)–Si(1)–C(12)	113.4(3)	C(2)–Si(4)–C(42)	113.8(3)
C(1)–Si(1)–C(13)	112.5(3)	C(2)–Si(4)–C(43)	108.6(4)
C(11)–Si(1)–C(12)	106.3(4)	C(41)–Si(4)–C(42)	104.3(4)
C(11)–Si(1)–C(13)	105.0(4)	C(41)–Si(4)–C(43)	103.6(5)
C(12)–Si(1)–C(13)	105.7(4)	C(42)–Si(4)–C(43)	109.4(4)
C(1)–Si(2)–C(21)	112.1(3)	C(2)–Si(5)–C(51)	111.9(3)
C(1)–Si(2)–C(22)	114.0(3)	C(2)–Si(5)–C(52)	115.9(4)
C(1)–Si(2)–C(23)	111.1(3)	C(2)–Si(5)–C(53)	108.5(5)
C(21)–Si(2)–C(22)	104.8(4)	C(51)–Si(5)–C(52)	108.0(4)
C(21)–Si(2)–C(23)	108.0(4)	C(51)–Si(5)–C(53)	106.2(5)
C(22)–Si(2)–C(23)	106.5(4)	C(52)–Si(5)–C(53)	105.7(6)
C(1)–Si(3)–C(31)	113.7(3)	C(2)–Si(6)–C(61)	109.3(4)
C(1)–Si(3)–C(32)	110.0(3)	C(2)–Si(6)–C(62)	116.4(4)
C(1)–Si(3)–C(33)	113.8(4)	C(2)–Si(6)–C(63)	111.7(3)
C(31)–Si(3)–C(32)	104.2(4)	C(61)–Si(6)–C(62)	105.1(5)
C(31)–Si(3)–C(33)	106.5(4)	C(61)–Si(6)–C(63)	105.8(4)
C(32)–Si(3)–C(33)	108.0(4)	C(62)–Si(6)–C(63)	107.8(4)
As(1)–C(1)–Si(1)	114.2(3)	As(2)–C(2)–Si(4)	100.3(3)
As(1)–C(1)–Si(2)	108.1(3)	As(2)–C(2)–Si(5)	109.2(3)
As(1)–C(1)–Si(3)	99.8(3)	As(2)–C(2)–Si(6)	112.0(3)
Si(1)–C(1)–Si(2)	111.7(3)	Si(4)–C(2)–Si(5)	111.7(3)
Si(1)–C(1)–Si(3)	111.9(3)	Si(4)–C(2)–Si(6)	110.4(3)
Si(2)–C(1)–Si(3)	110.6(3)	Si(5)–C(2)–Si(6)	112.6(3)

been established for As–As single bonds.[6] It therefore seems reasonable to regard 2.22—2.24 Å as the arsenic–arsenic double bond length. Interestingly the percentage shortening accompanying double bond formation is approximately constant for the heavier RE=E′R′ molecules (Table 4).

Further comparison of the structures of (**1**) and (**2**) reveals that there is a wide variation in arsenic bond angles. The trend, however, correlates with the steric demands of the alkyl or aryl residue since the As–As–C bond angles are 93.6(3), 99.9(3), and 106.3(2) (mean) for $(Me_3Si)_2CH$, 2,4,6-$Bu^t_3C_6H_2$, and $(Me_3Si)_3C$ groups, respectively.

The average As–As–C bond angle for (**2**) is approximately 2° less than that for the analogous diphosphene, $(Me_3Si)_3CP{=}PC(SiMe_3)_3$.[4] This angle diminution constitutes part of a general trend for the RE=E′R′ molecules (Table 4). Comparing identical substituents, it is clear that the R–E–E′ and E–E′–R′ bond angles decrease as the atomic number of E or E′ increases. The trend towards diminished bond angles with the heavier main-group elements is a widely recognised phenomenon and is illustrated, for example, by the H–E–H bond angles and pyramidal inversion barriers of EH_3 molecules (E = N, P, As, Sb, or Bi).[7] The strong pyramidality of the heavier molecules is usually explained on the basis of the inert *s*-pair effect.

Experimental

The diarsene, $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**) was prepared *via* the reaction of $AsCl_2[C(SiMe_3)_3]$ with $LiBu^t$ as described by Couret *et al.*[3] Careful attention must be paid to the purification of (**2**). This was accomplished by several successive chromatographic separations using a silica-gel column and n-hexane as eluant. Crystals of (**2**) suitable for *X*-ray diffraction experiments were grown from n-hexane solutions at −20 °C. It was important to carry out the *X*-ray study immediately because, even in sealed nitrogen-filled capillaries, (**2**) decomposes to a colourless material in a few days.

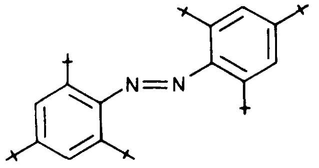
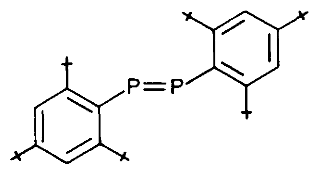
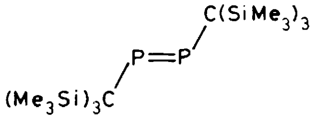
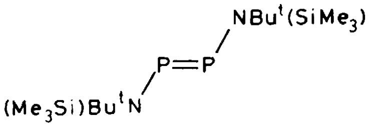
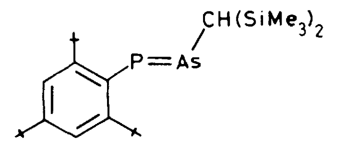
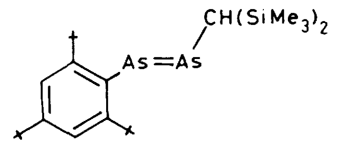
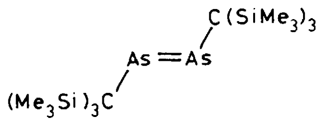
Crystal Structure Determination of $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**).—*Crystal data.* $C_{20}H_{56}As_2Si_6$, M = 615.02, triclinic, space group $P\bar{1}$ (no. 2), a = 9.151(3), b = 12.682(2), c = 15.537(4) Å, α = 70.07(2), β = 89.61(2), γ = 87.88(2)°, U = 1 694(2) Å^3, D_c = 1.203 g cm^{-3}, Z = 2, $F(000)$ = 652, Mo-K_α radiation (graphite monochromator), λ(Mo-K_α) = 0.710 69 Å.

Data collection, structure solution and refinement. A single crystal of (**2**) of size 0.4 × 0.3 × 0.2 mm was sealed in a Lindemann capillary under nitrogen and mounted on an Enraf–Nonius CAD4-F diffractometer. Initial lattice parameters were determined from a least-squares fit of 20 accurately centred

Table 3. Atomic positional parameters for $(Me_3Si)_3CAs{=}AsC(SiMe_3)_3$ (**2**) with estimated standard deviations in parentheses

	Molecule A				Molecule B		
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
As(1)	−0.006 2(2)	0.465 1(1)	0.076 70(8)	As(2)	0.467 5(2)	0.581 5(1)	0.509 58(8)
Si(1)	0.068 6(4)	0.228 3(3)	0.043 0(2)	Si(4)	0.414 3(6)	0.827 9(3)	0.409 8(3)
Si(2)	−0.251 4(4)	0.287 9(3)	0.093 8(2)	Si(5)	0.721 7(5)	0.721 5(4)	0.388 9(3)
Si(3)	0.007 2(4)	0.249 6(3)	0.237 3(2)	Si(6)	0.445 4(5)	0.676 1(3)	0.288 0(3)
C(1)	−0.045(1)	0.302 0(8)	0.109 0(7)	C(2)	0.518(1)	0.703 2(8)	0.393 1(6)
C(11)	0.262(1)	0.281(1)	0.019 4(9)	C(41)	0.420(2)	0.837(1)	0.529(1)
C(12)	−0.014(2)	0.242(1)	−0.073 6(8)	C(42)	0.478(2)	0.969(1)	0.333(1)
C(13)	0.093(2)	0.072(1)	0.107(1)	C(43)	0.207(2)	0.817(2)	0.388(1)
C(21)	−0.297(2)	0.142(1)	0.102(1)	C(51)	0.781(2)	0.818(1)	0.275(1)
C(22)	−0.327(1)	0.381(1)	−0.021 1(9)	C(52)	0.836(2)	0.592(1)	0.418(1)
C(23)	−0.361(2)	0.326(1)	0.184(1)	C(53)	0.772(2)	0.791(2)	0.477(1)
C(31)	−0.053(2)	0.349(1)	0.298 5(8)	C(61)	0.589(2)	0.585(1)	0.249(1)
C(32)	0.214(2)	0.238(1)	0.251(1)	C(62)	0.278(2)	0.601(1)	0.303(1)
C(33)	−0.068(2)	0.108(1)	0.305(1)	C(63)	0.419(2)	0.811(1)	0.186 9(9)

Table 4. Bond lengths (Å) and angles (°) for RE=E′R′ molecules

Compound	R–E–E′ or R′–E′–E/°	E=E′/Å	Sum of double-bond covalent radii (Å)[a]	E–E′/Å	Shortening (%)
	113.2 113.7 [b]	1.257[b]		1.451[c]	13
	102.8(1)[d]	2.034(2)[d]	2.00	2.21[c]	8
	108.2(4) 108.9(4) [e,f] 108.9(2) 108.1(2) [e,g]	2.014(6) 2.004(6) [e,f] 2.001(3) 2.003(2) [e,g]	2.00	2.21[c]	9
	102.2[h]	2.034[h]	2.00	2.21[c]	8
	96.4(2)[i,j] 101.2(2)[i,k]	2.124(2)[i]	2.11	2.32—2.36[l]	9—10
	93.6(3)[m,n] 99.9(3)[m,o]	2.224(2)[m]	2.22	2.43—2.46[p]	9—10
	106.2(2) 106.4(2) [e,q]	2.243(1) 2.245(1) [e,q]	2.22	2.43—2.46[p]	9—10

[a] Ref. 5. [b] Y. LePage, E. J. Gabe, Y. Wang, L. R. C. Barclay, and H. L. Holm, *Acta Crystallogr., Sect. B.*, 1980, **36**, 2846. [c] 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' ed. L. E. Sutton, Chemical Society Special Publications, Numbers 11 and 18, 1958 and 1965. [d] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 1981, **103**, 4587. [e] Two crystallographically independent molecules per asymmetric unit. [f] Ref. 4. [g] J. Jaud, C. Couret, and J. Escudie, *J. Organomet. Chem.*, 1983, **249**, C 25; J. Escudie, C. Couret, H. Ranaivonjatovo, J. Satge, and J. Jaud, *Phosphorus Sulphur*, 1983, **17**, 221. [h] E. Niecke, R. Ruger, M. Lysek, S. Pohl, and W. Schoeller, *Angew. Chem.*, 1983, **95**, 495; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 486. [i] A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski, and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.*, 1983, 881. [j] P–As–C. [k] C–P–As. [l] W. S. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 1789; M. Bandler, Y. Atkalay, T. Heinlein, and K-F. Tebbe, *Z. Naturforsch., Teil B*, 1982, **37**, 299. [m] Ref. 2. [n] As–As–C(alkyl). [o] As–As–C(aryl). [p] A. L. Rheingold and P. J. Sullivan, *Organometallics*, 1983, **2**, 327. [q] This work.

reflections and subsequently refined using higher angle data, $15 \leqslant 2\theta \leqslant 35°$. These indicated a triclinic lattice.

Data were collected in the range $2.0 < 2\theta < 45°$ using the ω—2θ scan mode for one independent half $+h$, $\pm k$, $\pm l$. The ω scan angle was determined according to the formula $A + B \tan \theta$ where A and B were set to 0.8 and 0.35, respectively. Detector aperture settings were determined in a like manner with $A = 4.0$ and $B = 1.0$. The final scan speed was calculated on the basis of the net intensity gathered in an initial pre-scan and ranged from 6.7 to 1.8° min^{-1}. Two check reflections were measured every 30 min throughout the 51 h of data collection and showed a 40% decrease in intensity. This was a result of the apparent thermal instability of (**2**), but the decay was approximately linear with time.

Data were corrected for the effects of Lorentz, polarisation, and decay but not for absorption, $\mu = 21.8\ \text{cm}^{-1}$. From a total of 4 075 unique measured reflections, 2 875 were considered observed, $I > 3.0\sigma(I)$, and used in the structure solution and refinement. The two arsenic atoms were located from a Patterson map and refined in the space group $P\bar{1}$. This choice of space group was confirmed by subsequent refinement. All other non-hydrogen atoms were located from subsequent difference-Fourier maps and refined by full-matrix least squares with anisotropic thermal parameters. Hydrogen atoms were neither located nor refined but were placed in calculated positions with a fixed isotropic thermal parameter ($B = 4.0$ Å^2) and included in the structure factor calculation.

The asymmetric unit comprises two crystallographically independent halves of (**2**) related to their respective other halves by a centre of inversion. For molecule B the final difference-Fourier map showed three peaks of *ca.* 1.5 e Å^{-3}. These were all *ca.* 1.85 Å from C(2) with angles at C(2) of *ca.* 112° and therefore probably represent three silicon atoms in an orientation of low occupancy which differs from the major conformation observed. No peaks indicative of their corresponding methyl carbons were observed and refinement of these silicons with suitable occupancy factors proved unsuccessful and was subsequently omitted. No other chemically significant peaks were present. A weighting scheme was introduced to down-weight intense reflections and was of the form $w = [4F^2/\sigma^2(F^2) + P^2F^4]$ with $P = 0.06$. Final least-squares refinement converged smoothly to give residuals $R\ (= \Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0727$ and $R'\ \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\} = 0.0983$. Scattering factors were taken from ref. 8 and were corrected for anomalous dispersion.

Acknowledgements

We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

References

1 A. H. Cowley, *Polyhedron*, 1984, **3**, 389 and refs. therein.
2 A. H. Cowley, J. G. Lasch, N. C. Norman, and M. Pakulski, *J. Am. Chem. Soc.*, 1983, **105**, 5506.
3 C. Couret, J. Escudié, Y. Madaule, H. Ranaivonjatovo, and J-G. Wolf, *Tetrahedron Lett.*, 1983, **24**, 2769.
4 A. H. Cowley, J. E. Kilduff, N. C. Norman, M. Pakulski, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, 1983, **105**, 4845.
5 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
6 L. K. Maxwell, S. B. Hendricks, and V. M. Mosely, *J. Chem. Phys.*, 1935, **3**, 699; J. H. Burns and J. Waser, *J. Am. Chem. Soc.*, 1957, **79**, 859; K. Hedberg, E. W. Hughes, and J. Waser, *Acta Crystallogr.*, 1961, **14**, 369; A. L. Rheingold and P. J. Sullivan, *Organometallics*, 1983, **2**, 327.
7 W. Cherry, N. Epiotis, and W. T. Borden, *Acc. Chem. Res.*, 1979, **10**, 167.
8 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Received 10*th May* 1984; *Paper* 4/754