

Formation of a tetrazole from $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{I}$. Crystal structure of $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{N}-\text{N}=\text{C}(\text{Me})-\text{N}=\text{N}$

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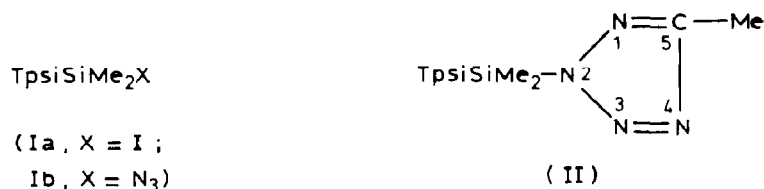
(Received January 29th, 1988)

Abstract

The iodide $(\text{Me}_2\text{PhSi})_3\text{CSiMe}_2\text{I}$ was found to react with MeCN in the presence of NaN_3 to give the $(\text{PhMe}_2\text{Si})_3\text{CSiMe}_2\text{N}-\text{N}=\text{C}(\text{Me})-\text{N}=\text{N}$, the structure of which was determined by an X-ray diffraction study. Some of the corresponding trimethylsilyl-substituted tetrazole was formed from Me_3SiI under similar conditions.

Introduction

We have previously reported that the iodide $\text{TpsiSiMe}_2\text{I}$ ($\text{Tpsi} = (\text{PhMe}_2\text{Si})_3\text{C}$) (Ia), behaves analogously to the related species $\text{TsiSiMe}_2\text{I}$ ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$) in reacting with NaN_3 in $(\text{MeOCH}_2\text{CH}_2)_2\text{O}$ and with KSCN in MeCN to give the simple substitution products $\text{TpsiSiMe}_2\text{N}_3$, (Ib), and $\text{TpsiSiMe}_2\text{NCS}$ [1]. However, we have now found that the iodide Ia unexpectedly reacts with NaN_3 in MeCN to give a tetrazole derivative, (II), whereas $\text{TsiSiMe}_2\text{I}$ under similar conditions is known to give the azide TsiMe_2N_3 [2].

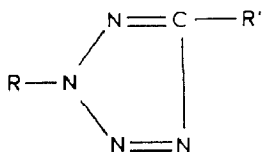


Results and discussion

A solution of the iodide Ia in MeCN was stirred under reflux with a molar equivalent of NaN_3 for 48 h then cooled and kept at -22°C . The white solid which separated was shown by elemental analysis, spectroscopy, and mass spectrometry to be a tetrazole derivative (isolated in 53% yield), but the data did not distinguish between the isomers II and III. Single crystal diffraction showed that it was in fact II.

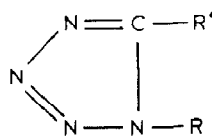
The prolonged reflux is evidently unnecessary for formation of II, since when the reaction was carried out on a smaller scale with an excess of NaN_3 and for only 6 h at room temperature the product was shown to be a mixture of unchanged Ia, the azide Ib, and the tetrazole II in ca. 20/27/53 ratio.

Since Me_3SiN_3 is known to add to some alkyl or aryl cyanides under suitable conditions to give trimethylsilyl-substituted tetrazoles [3–6], it seemed likely that in the formation of II, the iodide Ia first reacted with the NaN_3 to give the azide Ib, and the latter then added to the MeCN. However, even Me_3SiN_3 reacts with MeCN only under prolonged reflux or at $125\text{--}130^\circ\text{C}$ in the presence of AlCl_3 [4,5] (and with EtCN in a bomb at 150°C for 15 h [6]), and so we were not surprised to find that the azide Ib was recovered unchanged after 6 h refluxing of its solution in MeCN (or in MeCN containing NaI). It seemed possible that the reaction of the azide with the nitrile is facilitated by the presence of HI formed from Ia and traces of water in the MeCN, since protonation at the nitrogen atom of the latter might have an analogous effect to that of complexation with AlCl_3 . In keeping with this possibility we found that when a solution of Me_3SiI in MeCN was refluxed with NaN_3 for 4 d (probably an unnecessarily long time), analysis of the product mixture of GLC/MS indicated that $(\text{Me}_3\text{Si})_2\text{O}$, the tetrazole IVa, and trimethylsilyltetrazole (assumed to be) (IVb) were present in an ca. 80/15/5 ratio. (The disiloxane was presumably mainly produced during the analytical procedure, perhaps from Me_3SiN_3 as well as from the tetrazole IVb and Me_3SiI) during the analytical procedure. It is likely that the yield of tetrazole could be improved by appropriate modification of the conditions, but we were interested only in finding whether any tetrazole formation occurred).



(IVa, $\text{R}' = \text{Me}$; $\text{R} = \text{H}$;

IVb, $\text{R}' = \text{Me}$; $\text{R} = \text{SiMe}_3$)



(V)

In an attempt to confirm that the azide Ib would react with MeCN in the presence of HI, a solution of Ib and Me_3SiI (which would rapidly give some HI) in MeCN was refluxed with NaN_3 , but only unchanged Ib was recovered (though a little II could possibly have remained in the mother liquor after work-up). A further difficulty with attribution of the formation of II to catalysis by HI of the reaction of the azide Ib with MeCN is that no tetrazole was formed from $\text{TsiSiMe}_2\text{I}$ under the conditions that gave II even though $\text{TsiSiMe}_2\text{I}$ is known to react with MeCN containing traces of water to give the hydroxide [2]. However, since methanolysis of

Ia is markedly faster than that of $\text{TsiSiMe}_2\text{I}$, whereas the two iodides react with salts at rather similar rates [1], less HI might be generated from $\text{TsiSiMe}_2\text{I}$ in MeCN in the presence of NaN_3 .

Another possible route to formation of a tetrazole from Me_3SiI and from Ia which had to be considered is one involving initial reaction (presumably reversible) of the iodide with MeCN to give the nitrilium salt $[\text{RSiMe}_2\text{N}\equiv\text{CMe}][\text{I}]$ ($\text{R} = \text{Me}$ or Tpsi), followed by reaction of the latter with NaN_3 . (Since such reaction of a silicon iodide with MeCN would show some analogy to methanolysis, it would not be surprising if Ia formed the nitrilium salt more rapidly than $\text{TsiSiMe}_2\text{I}$, which would thus have a greater opportunity to form the azide, which on this interpretation would be inert.) This possibility was suggested by the facts that (a) Me_3SiI has been considered by Olah and his colleagues to react with MeCN to give the salt $[\text{Me}_3\text{SiN}\equiv\text{CMe}][\text{I}]$ [7], and (b) the nitrilium salts $[\text{RN}\equiv\text{CR}'][\text{BF}_4]$ ($\text{R} = \text{alkyl}$) (unlike the parent $\text{R}'\text{C}\equiv\text{N}$ species) react with NaN_3 to give tetrazoles [8]. There are two major obstacles, however, to acceptance of this route. The first is that Bassindale and Stout have concluded that no adduct is, in fact, formed between Me_3SiI and MeCN [9] (though reversible formation of a very small amount of the nitrilium salt cannot be ruled out), and, furthermore, even the perchlorate $\text{Ph}_3\text{SiOCIO}_3$ seems not to react with MeCN [10]. The second objection is that addition of NaN_3 to the nitrilium ion $[\text{>SiN}\equiv\text{CMe}]^+$ should (cf. ref. 8) give a 1,5-disubstituted tetrazole, e.g. III, not the observed 2,5-product. It is conceivable that an initially formed 1,5-product could rearrange to the 2,5-isomer under the conditions used (involving the presence of HI), but such a migration seems less likely for the $(\text{Me}_2\text{PhSi})_3\text{C}$ than for the Me_3Si group.

Further studies would be needed to establish the mechanism of formation of II from Ia and NaN_3 in MeCN, and we are not in a position to undertake them.

Structure of the tetrazole product

Spectroscopic properties do not normally allow firm distinction between isomeric disubstituted tetrazoles, e.g. between II and III, or between IV and V. Washburne and Peterson assumed (probably correctly in view of our results) that the reaction of the nitriles ArCN ($\text{Ar} = \text{aryl}$) with Me_3SiN_3 gave initially 2,5-disubstituted tetrazoles of type IV ($\text{R}' = \text{Me}_3\text{Si}$), rather than their 1,5-disubstituted analogues, V [3]. The 2,5-isomers IV ($\text{R}' = \text{Et}$, Ph , or CH_2Ph ; $\text{R} = \text{SiMe}_3$) were also said to be formed from reactions of the $\text{R}'\text{CN}$ species with Me_3SiN_3 at $150\text{--}160^\circ\text{C}$ [6], and IV ($\text{R}' = \text{Ph}$, $\text{R} = \text{SiMe}_3$) was judged to be formed from 5-phenyltetrazole IV ($\text{R}' = \text{Ph}$, $\text{R} = \text{H}$) and $(\text{Me}_3\text{Si})_2\text{NH}$ [11]. However, Sinitza et al. assigned the 4,5-structure V ($\text{R}' = \text{Ph}$, $\text{R} = \text{SiMe}_3$) to the product from PhCN and Me_2SiN_3 in the presence of AlCl_3 [4]. In order to leave no doubt about the structure of the product from the iodide Ia, NaN_3 , and MeCN we carried out an X-ray diffraction study.

The structure determination was complicated by the fact that the space-filling characteristics of the 5-methyltetrazolyl group are sufficiently similar to that of a phenyl group to give rise to disorder involving the heterocyclic and one of the phenyl groups, with 50/50 site occupancies. (It will be appreciated that the disorder must actually involve the $\text{SiMe}_2\text{CN}_4\text{Me}$ and SiMe_2Ph ligands, but is apparent only for the ring systems, the positions of the atoms of the two SiMe_2 systems being effectively identical in the contributing forms.) This disorder led to high R and R'

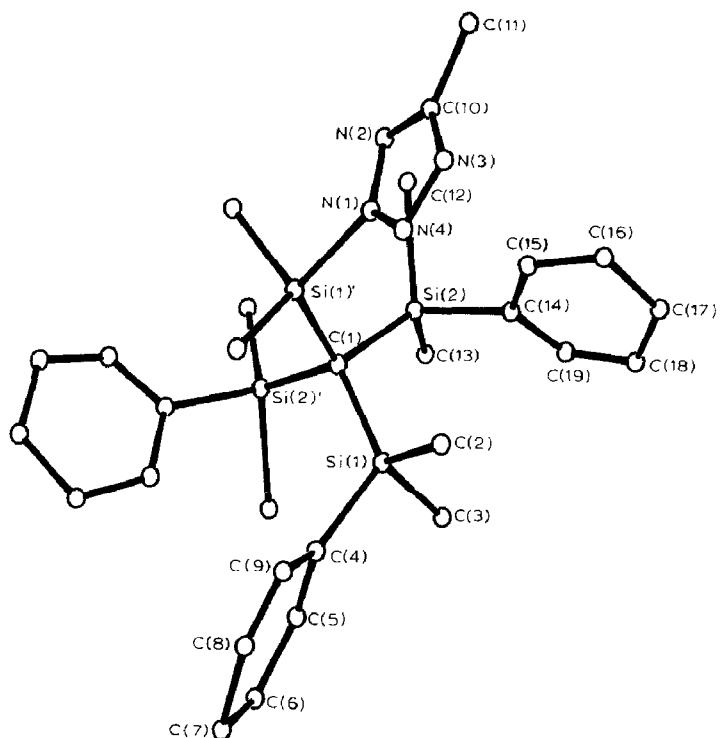


Fig. 1. The molecular structure of II showing the atom numbering.

values (see Experimental section), and no reliable parameters could be derived for the heterocyclic ring system, but the TpsiSiMe₂ and Me substituents were shown unambiguously to be at the 2- and 5-positions of the ring, respectively (see Fig. 1).

Caution is necessary in considering the detail of the molecular parameters shown in Table 2 in view of the disorder and high *R* value, but it does seem that in the crystal the Si(1)–C(1) bond (1.960(2) Å) is distinctly longer than the Si(2)–C(1) bond (1.911(2) Å), and the Si(2)–C(12) (1.942(2) Å) bond is longer than the adjacent Si(2)–C(13) bonds (1.879(3) Å).

Experimental

The iodide Ia was prepared as previously described [1]. Acetonitrile was dried by refluxing with and distillation from CaH₂ and stored over 4 Å molecular sieve; however, it evidently contained some water, since when a solution of Ia (0.1 g) in the solvent (10 cm³) was refluxed for 6 h and the solid removed, the residue was shown by GLC-MS to be a mixture of Ia and TpsiSiMe₂OH.

Reaction of Ia with MeCN

(a) A mixture of Ia (2.0 g, 3.32 mmol), NaN₃ (0.22 g, 3.40 mmol), and MeCN (200 cm³) under N₂ was boiled under reflux for 48 h, then cooled and kept at –22 °C for 4 d. The solid which had separated was essentially pure 2-[tris(dimethylphenylsilyl)methyl]-5-methyltetrazole (0.98 g, 53%), m.p. 161 °C (Found: C, 62.3; H, 7.9; N, 9.6. C₂₈H₄N₄Si₄ calc: C, 62.4; H, 7.5; N, 10.0%); δ(H) (CCl₄) 0.63 (18H, s,

SiMe₂Ph), 0.85 (6H, s, SiMe₂N), 2.55 (3H, SiCMe), 6.8–7.4 (15H, m, Ph); δ (C) (CDCl₃) 5.3 (s, SiMe₂Ph), 6.4 (s, SiMe₂N), 10.4 (s, Me), 127.3–139.6 (Ph), and 161.8 (NCN); m/z 558 ($[M]^+$), 543 ($[M - \text{Me}]^+$), 530 ($[M - \text{N}_2]^+$), 481 ($[M - \text{Ph}]^+$), 439, 397, 381, 325, 309, 197 ($[\text{Ph}_2\text{MeSi}]^+$) and 135 ($[\text{PhMe}_2\text{Si}]^+$).

No attempt was made to recover further material from the mother liquor.

(b) A mixture of Ia (0.10 g, 0.166 mmol), NaN₃ (0.033 g, 0.50 mmol), and MeCN (10 cm³) was stirred at room temperature for 6 h. Removal of the solvent under reduced pressure left a solid, which was dissolved in CCl₄. The solution was shaken with water then separated, dried (MgSO₄), and evaporated. The residual solid was shown by ¹H NMR spectroscopy and by linked GLC-MS to be a mixture of Ia, the azide Ib, and the tetrazole II in ca. 20/27/53 ratio.

Treatment of the azide Ib with NaN₃ in the presence of Me₃SiI

A mixture of Ib (0.53 g, 0.95 mmol), Me₃SiI (0.95 mmol), and NaN₃ (1.25 mmol), in MeCN (50 cm³) was stirred under reflux for 24 h then cooled and kept at –22 °C for 24 h. The white solid which separated was shown by its NMR spectrum to be unchanged Ib (ca. 0.35 g, 66%), and there were no detectable signals from the tetrazole II.

Reactions of Me₃SiI with NaN₃ in MeCN

A mixture of Me₃SiI (5 mmol), NaI (7.5 mmol), and MeCN (15 cm³) was stirred under reflux for 4 d. The solution was then cooled and examined by GLC-MS, which revealed the presence of three components in 80/15/5 ratio, and these appeared respectively to be: (Me₃Si)₂O, m/z 147 (base peak, $[M - \text{Me}]^+$); 5-methyltetrazole, (IVa), m/z 84 ($[M]^+$); and the tetrazole IVb, m/z 156 (2%, $[M]^+$), 128 (10, $[M - \text{N}_2]^+$), 100 (40, $[M - 2\text{N}_2]$), and 73 (100, $[\text{Me}_3\text{Si}]^+$).

Structure determination

Crystal data

C₂₉H₄₃N₄Si₄, M 560.0, orthorhombic, space group $P2_12_12$, a 14.557(4), b 11.767(6), c 9.034(4) Å, U 1547.5 Å³, Z = 2, D_c 1.20 g cm⁻³, $F(000)$ 602. Monochromated Mo- K_α radiation, λ 0.71069 Å, μ 2.11 cm⁻¹. Space group from systematic absences of $h00$ for h odd and $0k0$ for k odd.

Data were obtained with an Enraf–Nonius CAD4 diffractometer from a crystal of dimensions 0.35 × 0.20 × 0.25 mm. Intensities for hkl reflections with $2 < \theta < 22^\circ$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta$ (1.20 + 0.35 tan θ) and a maximum time of 1 min. Two standard reflections monitored every 30 min showed no significant variation. Data were corrected for Lorentz and polarization effects but not for absorption, and after averaging of equivalent reflections 724 (out of an initially recorded 1135) reflections with $|F|^2 > \sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.021I)^2]^{1/2}/Lp$.

The structure was solved by direct methods with the MULTAN program [12]. Scattering factors for neutral atoms were taken from ref. 13. In space group $P2_12_12$ with Z = 2 the molecule must lie on a 2-fold rotation axis. The molecule at first appeared to be (PhMe₂Si)₄C with two crystallographically independent phenyl groups, but from the refinement one of the phenyl groups appeared to have high temperature factors, and this was assumed to be due to disorder between a phenyl

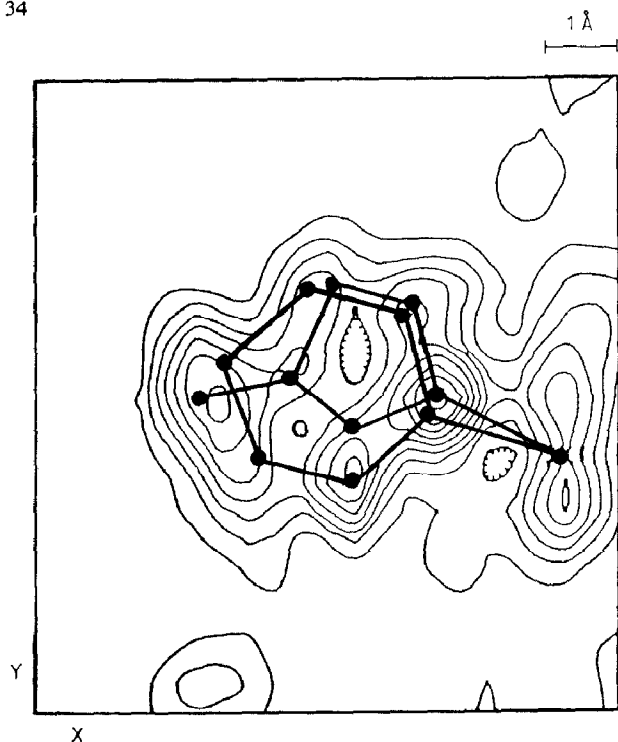


Fig. 2. The difference electron density map in the plane of the disordered phenyl and tetraazole group showing the overlapping of the groups.

Table 1

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Si(1)	4434(4)	1164(6)	7564(10)
Si(2)	4034(4)	-573(5)	5087(9)
N(1)	5276	2294	8467
N(2)	5445	3155	7743
N(3)	6057	3100	9806
N(4)	5632	2176	9687
C(1)	5000	0	6309(44)
C(2)	3786(18)	589(24)	9179(34)
C(3)	3629(16)	2135(19)	6480(37)
C(4)	5193	2267	8394
C(5)	5418	3270	7799
C(6)	5917	4264	8045
C(7)	6294	4227	9427
C(8)	6043	3170	10074
C(9)	5578	2174	9741
C(10)	5991	3732	8624
C(11)	6409	4724	8564
C(12)	5713(17)	2092(18)	4353(32)
C(13)	3828(15)	297(18)	3375(29)
C(14)	2868(15)	-700(18)	5965(31)
C(15)	2705(15)	-1539(20)	7164(37)
C(16)	1808(14)	-1707(17)	7792(31)
C(17)	1096(15)	-963(19)	7284(36)
C(18)	1257(14)	-137(20)	6159(33)
C(19)	7871(15)	38(19)	5572(31)

and a tetrazole group. The structure factors were calculated with omission of this Ph/tetrazole group, and a different map calculated. The electron density map drawn out in the plane of the phenyl/tetrazole group was found to be consistent with overlap of the phenyl and tetrazole groups, as can be seen from Fig. 2. Approximate atom coordinates were derived for all the non-hydrogen atoms in the two groups, and these were included with 0.5 occupancies. For the least-squares refinement the rings in the overlapping phenyl and tetrazole groups were restrained to be planar with bond lengths equal to the sums of the relevant covalent radii, and when the parameters for these groups reached convergence they were fixed and the remaining non-hydrogen atoms in the molecule were refined anisotropically by full matrix least-squares. No attempt was made to include hydrogen atoms. Refinement

Table 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Si(1)–C(1)	1.960(2)	Si(2)–C(1)	1.911(2)
Si(1)–C(2)	1.864(3)	Si(1)–C(3)	1.907(3)
Si(1)–N(1)	1.984	Si(1)–C(4)	1.862
Si(2)–C(12)	1.942(2)	Si(2)–C(13)	1.879(3)
Si(2)–C(14)	1.880(2)	C(14)–C(15)	1.484(4)
C(14)–C(19)	1.375(3)	C(15)–C(16)	1.438(3)
C(16)–C(17)	1.432(3)	C(17)–C(18)	1.427(4)
C(18)–C(19)	1.380(4)	N(1)–N(2)	1.231
N(3)–N(4)	1.256	N(1)–N(4)	1.226
N(2)–C(10)	1.313	C(7)–C(8)	1.422
N(3)–C(10)	1.305	C(10)–C(11)	1.317
C(4)–C(9)	1.344	C(4)–C(5)	1.337
C(6)–C(7)	1.365	C(5)–C(6)	1.395
C(8)–C(9)	1.386		
C(1)–Si(1)–C(2)	114.30(1)	C(1)–Si(1)–C(3)	112.35(1)
C(1)–Si(1)–N(1)	117	C(1)–Si(1)–C(4)	118(1)
C(2)–Si(1)–C(3)	108(1)	C(2)–Si(1)–N(1)	104
C(2)–Si(1)–C(4)	104	C(3)–Si(1)–N(1)	101
C(3)–Si(1)–C(4)	99	Si(1)–C(1)–Si(2)	113.40(3)
C(1)–Si(2)–C(12)	112.50(8)	C(1)–Si(2)–C(13)	114(1)
C(1)–Si(2)–C(14)	117(1)	C(12)–Si(2)–C(13)	105(1)
C(12)–Si(2)–C(14)	104(1)	C(13)–Si(2)–C(14)	104.26(1)
Si(1)–C(1)–Si(1) ^a	109(1)	Si(1)–C(1)–Si(2)	105.75(3)
C(4)–C(9)–C(8)	109(1)	Si(2)–C(1)–Si(2) ^a	109(1)
Si(2)–C(14)–C(15)	120(1)	Si(2)–C(14)–C(19)	124(1)
C(15)–C(14)–C(19)	116(1)	C(14)–C(15)–C(16)	122(1)
C(15)–C(16)–C(17)	117(1)	C(16)–C(17)–C(18)	122(1)
C(17)–C(18)–C(19)	119(1)	C(14)–C(19)–C(18)	125(1)
Si(1)–N(1)–N(2)	117	Si(1)–N(1)–N(4)	124
N(1)–N(2)–C(10)	103	N(2)–N(1)–N(4)	119
N(4)–N(3)–C(10)	113	N(1)–N(4)–N(3)	101
N(2)–C(10)–C(11)	135	N(2)–C(10)–N(3)	104
N(3)–C(10)–C(11)	120	Si(10)–C(4)–C(9)	124
Si(1)–C(4)–C(5)	127	C(5)–C(4)–C(9)	109
C(4)–C(5)–C(6)	143	C(5)–C(6)–C(7)	109
C(6)–C(7)–C(8)	108	C(7)–C(8)–C(9)	140

^a Symmetry element $'$ is $1 - x, -y, z$.

converged at $R = 0.110$, $R' = 0.130$ when the maximum shift to error ratio was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was featureless.

Atom coordinates are listed in Table 1, and bond angles and distances in Table 2. Lists of thermal parameters and structure factors are available from the authors.

Acknowledgements

We thank the S.E.R.C. for support (via C.E.), the Ministry of Higher Education of the Kingdom of Saudi Arabia for the award of a postgraduate scholarship to A.I.M., the Ministry of Higher Education of Iraq for the award of a postgraduate scholarship to N.H.B., Mr. A.M. Greenway and Mr. A. Adams for mass spectra, and Dr. A.G. Avent and Mr. B.D. Meadows for NMR spectra.

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