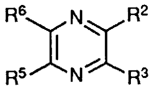
Radical Cations and Anions of Pyrazines: An Electron Paramagnetic Resonance Study

Uwe Eiermann,[a] Franz A. Neugebauer,*,[a] Harish Chandra,[b] Martyn C. R. Symons*,[b] and Jane L. Wyatt[b]
[a] *Abt. Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstr. 29, D 6900 Heidelberg, Germany*
[b] *Department of Chemistry, The University, Leicester LE1 7RH, UK*

Dilute solutions of a series of pyrazines (**1**–**13**) in $CFCl_3$ at 77 K were exposed to ^{60}Co γ-rays, generating the corresponding radical cations which were identified by their EPR spectra. Two distinct types of spectra were observed. Those obtained from mono- and di-methyl derivatives showed large hyperfine coupling to two ^{14}N nuclei similar to that of the parent pyrazine cation and are assigned to n(σ)-radical cations. The other spectra observed for the tetramethyl, OCH_3, SCH_3 and NR_2 derivatives are assigned to π-radical cations. These findings confirm that the SOMO has switched from n(σ) to π between the dimethyl derivatives **4**, **6** and **8** and the tetramethyl compound **9**, respectively. The NR_2-substituted radical cations $\mathbf{12}^{\bullet+}$ and $\mathbf{13}^{\bullet+}$ were also observed in fluid solution. The corresponding radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{13}^{\bullet-}$, studied in solid solution, show major hyperfine coupling to the two ring ^{14}N nuclei. Studies in fluid solution indicate that strong electron donor substituents (OCH_3, SCH_3, NR_2) convert the S-type π-SOMO of the pyrazine radical anion to a π-SOMO with predominant A-type character.

Appropriate substitution in various N-heterocycles, *e.g.* by alkyl or π-electron donating groups inverts the order of the highest filled n(σ)- and π-MOs. Recent EPR studies of radical cations obtained from substituted pyridines,[1] s-tetrazines[2] and benzo-[*c*]cinnolines[3] have clearly traced the switch in the wave function from σ to π. These radical cations are readily generated by γ-irradiation of dilute solutions of the molecular precursors in Freon or other fluorinated solvents.[4–9] We have now extended these studies to a series of pyrazines **1**–**13**. The photoelectron (PE) spectra of pyrazine (**1**),[10] 2,6-dimethylpyrazine (**8**),[11] and 2,3,5,6-tetramethylpyrazine (**9**)[12] indicate a reversal in the sequence of the two highest occupied MO's. Based on the shape of the first band in the PE spectra, and on calculations, the HOMO in **1** and **8** is n_+ while in **9** it is π(A, b_{2g}).[12] In agreement with this finding **1** generates a σ-radical cation on γ-irradiation.[4,13] In the PE spectra of **8** and **9**, however, the first two bands are very close and superpose.

We report EPR results for the radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{13}^{\bullet+}$ which have been generated by exposing dilute solutions of the precursors **1**–**13** in $CFCl_3$ to ^{60}Co γ-rays at 77 K. In the liquid phase, EPR spectra of radical cations could only be observed for $\mathbf{12}^{\bullet+}$ and $\mathbf{13}^{\bullet+}$. To our knowledge, the radical anions in this series have never been investigated by solid state EPR spectroscopy. Thus, we set out to compare the structures of the radical cations to those of the corresponding radical anions. In fluid solution the radical anions $\mathbf{1}^{\bullet-}$,[14] $\mathbf{4}^{\bullet-}$,[15] $\mathbf{6}^{\bullet-}$,[16] $\mathbf{8}^{\bullet-}$ [16,17] and $\mathbf{9}^{\bullet-}$ [17,18] have already been studied. In addition we now report EPR data of $\mathbf{5}^{\bullet-}$, $\mathbf{7}^{\bullet-}$, $\mathbf{10}^{\bullet-}$, $\mathbf{12}^{\bullet-}$ and $\mathbf{13}^{\bullet-}$ in fluid solution.



	R^2	R^3	R^5	R^6
1	H	H	H	H
2	CH_3	H	H	H
3	CD_3	H	H	H
4	CH_3	CH_3	H	H
5	CD_3	CD_3	H	H
6	CH_3	H	CH_3	H
7	CD_3	H	CD_3	H
8	CH_3	H	H	CH_3
9	CH_3	CH_3	CH_3	CH_3
10	OCH_3	H	OCH_3	H
11	SCH_3	H	SCH_3	H
12	$N(CH_3)_2$	H	$N(CH_3)_2$	H
13	$\overline{NCH_2CH_2CH_2CH_2}$	H	$\overline{NCH_2CH_2CH_2CH_2}$	H

Results and Discussion

Methyl Substituted Radical Cations $\mathbf{1}^{\bullet+}$–$\mathbf{9}^{\bullet+}$.—Our results clearly establish that all mono- and di-methyl derivatives of pyrazine form N-centred σ-radicals on electron loss. Under the conditions used, only the primary radical cations are expected. The presence of two equivalent strongly coupled nitrogen nuclei having large isotropic hyperfine coupling constants (Table 1, Fig. 1) rules out the alternative π-cations. Furthermore, had the

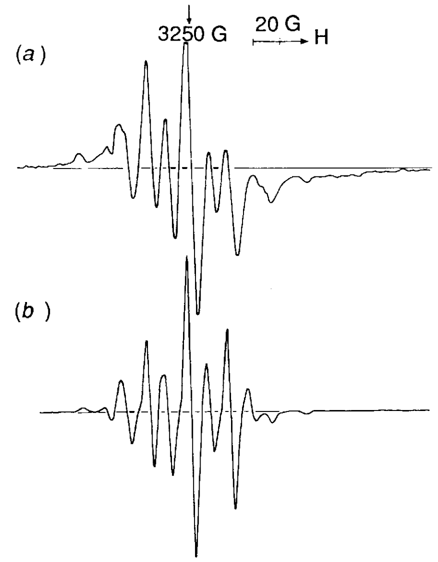


Fig. 1 (*a*) First derivative X-band EPR spectrum for 2,5-dimethylpyrazine **6** in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding σ-radical cation $\mathbf{6}^{\bullet+}$, together with (*b*) a simulation using the data in Table 1

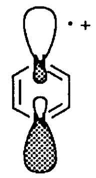
Table 1 ^{14}N and ^{1}H hyperfine coupling constants for pyrazine radical cations in $CFCl_3$ at 77 K together with approximate orbital populations (%)[a] on each nitrogen; (*i*) n(σ)-type, (*ii*) π-type

Radical	N_i	$A_{\parallel}/G^b$	$A_{\perp}/G$	A_{iso}/G	$2B$	a_s^2	a_p^2
(*i*)[c] $\mathbf{1}^{\bullet+d}$	2 N	32.7	18.4	23.2	9.5	4.2	29
	4 H(av)			30.6			
$\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$	2 N	31	17	21.7	9.3	3.9	28
	3 H(av)			30			
$\mathbf{4}^{\bullet+}$, $\mathbf{5}^{\bullet+}$	2 N	29	15	19.7	9.3	3.5	28
	2 H(av)			29			
$\mathbf{6}^{\bullet+}$, $^{e}\mathbf{7}^{\bullet+}$	2 N	28	16	20.0	8.0	3.6	24
	2 H(av)			30			
$\mathbf{8}^{\bullet+f}$	1 N 1 N	29	15	19.7	9.3	3.5	28
	2 H(av)			28			
(*ii*) $\mathbf{9}^{\bullet+}$	12 H^{β}			4			
$\mathbf{10}^{\bullet+g}$	6 H^{β}			4.5			
$\mathbf{11}^{\bullet+g}$	6 H^{β}			7.0			
$\mathbf{12}^{\bullet+g}$	2 N^{α}	*ca.* 21	*ca.* 0	7.23^h			
	12 H^{γ}			*ca.*7.5			

[a] Using atomic parameters given in ref. 19. [b] $G = 10^{-4}$ T. [c] (i) ± 0.5 G; $g_{\parallel} = 2.0024$, $g_{\perp}$ *ca.* 2.004. [d] Ref. 4; $g_x = 2.0024$, $g_y = 2.0034$, $g_z = 2.0023$. [e] Extra splitting of *ca.* 3 G probably from CH_3 protons. [f] ± 1.0 G. [g] Ring proton splitting not resolved in solid-state spectra. [h] Liquid-phase result.

cation been a π- rather than a σ-radical, one would have expected strong hyperfine coupling to the methyl protons. Use of the CD_3 derivatives, **3**, **5** and **7**, has established the complete absence of detectable splittings from any of the methyl protons. This is expected for the σ-radical cations, since the methyl protons are in γ-positions relative to the orbitals on nitrogen, so coupling is expected to be small. Again in accord with the σ-structures, substitution of $\mathbf{1}^{\bullet+}$ by methyl groups (as in $\mathbf{2}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, $\mathbf{6}^{\bullet+}$, $\mathbf{8}^{\bullet+}$) leads to a decrease in the number of equivalent (or nearly equivalent) coupled ring protons from 4 to 2.

For the mono- and di-methyl derivatives, the ^{14}N hyperfine parameters are all close to those of the parent pyrazine radical cation ($\mathbf{1}^{\bullet+}$).[4,13] Analysis of the EPR parameters in the normal way[19] gives *ca.* 4% 2s character on each nitrogen for the isotropic coupling, and *ca.* 30% 2p character for the anisotropic coupling. This analysis suggests that *ca.* 68% of the SOMO is comprised of sp-hybrid orbitals on nitrogen. The large ^{1}H hyperfine coupling of *ca.* 30 G indicates that hyperconjugative delocalisation into the C–H bonds accounts for the remaining spin-density.



Although the mono- (**2**) and the three di-methyl derivatives (**4**, **6** and **8**) give radical cations closely resembling the parent pyrazine radical cation, there is a remarkable change on going to the tetramethyl derivative (**9**). The spectra for the tetramethyl derivative are clearly not due to σ-radicals, but can readily be interpreted in terms of a π-radical with strong hyperfine coupling to many (at least ten) equivalent protons (Fig. 2). Thus the inversion of levels predicted from photoelectron spectroscopy is fully confirmed by our EPR results.

The proton hyperfine coupling constants for the σ-cations $\mathbf{1}^{\bullet+}$–$\mathbf{8}^{\bullet+}$ show no clear trend within the limits of resolution of the broad spectral features. The spectral features of the three dimethyl isomers are remarkably similar. Extra splittings of the inner components of the 2,6-dimethyl derivative ($\mathbf{8}^{\bullet+}$) suggest that the two nitrogen atoms are no longer exactly equivalent, and the best fit so far obtained is based on a small difference (Table 1). However, the sum of the ^{14}N coupling constants remains the same.

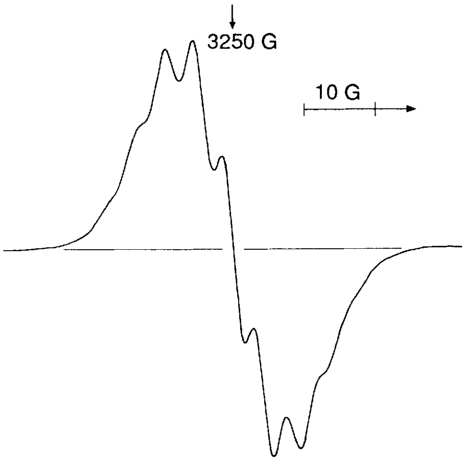


Fig. 2 First derivative X-band EPR spectrum for 2,3,5,6-tetramethylpyrazine **9** in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the corresponding π-radical cation $\mathbf{9}^{\bullet+}$

Shida and co-workers[4b] have noted distinct changes in the spectra of diazabenzene radical cations with temperature. We have also noted such changes, which are quite marked for pyrazine radical cations. We have been unable to interpret these changes in terms of any specific rotational behaviour. In particular, by far the most probable initial rotation, the in-plane mode, is not uniquely observable. It seems to us that in some temperature region general vibration sets in giving rise to well-defined spectral changes. It is noteworthy that methyl substitution strongly inhibits this motional averaging.

π-Radical Cations $\mathbf{9}^{\bullet+}$–$\mathbf{13}^{\bullet+}$.—The switch in the wave function from n(σ) to π lies undoubtedly between the dimethyl derivatives **4**–**8**, and the tetramethyl compound **9**, respectively. The solid-state spectrum of $\mathbf{9}^{\bullet+}$ shows at least eleven lines (*ca.* 4 G) clearly assignable to the twelve CH_3 protons. For $\mathbf{10}^{\bullet+}$ and $\mathbf{11}^{\bullet+}$ septet splittings were observed which we attribute to the coupling of the OCH_3 and SCH_3 protons, respectively. The $N(CH_3)_2$-substituted derivative **12** gave rise to a spectrum showing twelve protons with a coupling of *ca.* 7.5 G and lines which we tentatively attribute to the parallel features of the two $^{14}N^{\alpha}$ nuclei ($A_{\parallel}$ *ca.* 21 G). Perpendicular $^{14}N^{\alpha}$ features were not

Table 2 Isotropic hyperfine coupling constants for the radical cations **12**$^{\cdot+}$ and **13**$^{\cdot+}$ in ethanol–dichloromethane (9 : 1) at 230 K

	Method	$a(H^{3,6})$/G	$a(N^{\alpha})$/G	$a(H^{\gamma})$/G	$a(H^{\gamma})$/G	g
12$^{\cdot+}$	EPR	3.93	7.23 (2 N)	7.80 (6 H)	7.23 (6 H)	2.0031
	ENDOR	4.07		7.88	7.23	
13$^{\cdot+}$	EPR	4.05	7.15 (2 N)	11.15 (4 H)	10.40 (4 H)	2.0031
	ENDOR[a]	4.20		11.43	10.55	

[a] At 210 K.

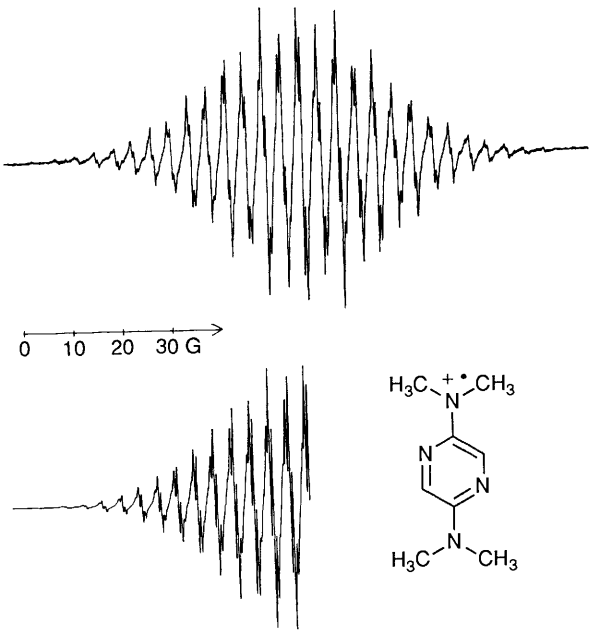


Fig. 3 First derivative X-band EPR spectrum for the radical cation of 2,5-bis(dimethylamino)pyrazine **12**$^{\cdot+}$ in ethanol–dichloromethane (9 : 1) at 230 K together with a simulation using the data given in Table 2

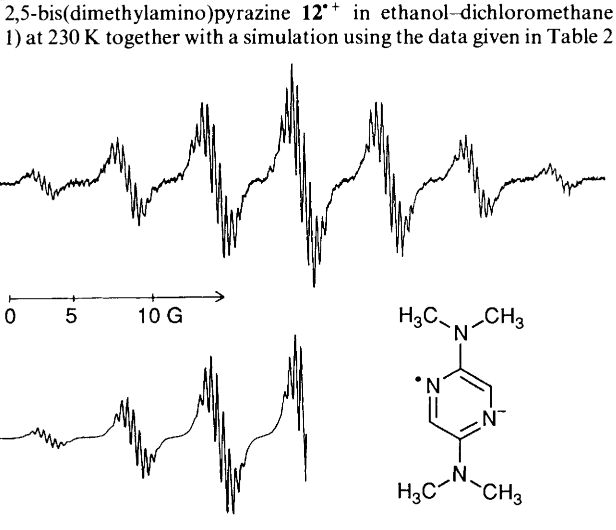


Fig. 4 First derivative X-band EPR spectrum for the radical anion of 2,5-bis(dimethylamino)pyrazine **12**$^{\cdot-}$ in DME at 300 K together with a simulation using the data in Table 4

observed but can be estimated from $A_{\parallel}$ and the $A_{\text{iso}}(^{14}N^{\alpha})$ value obtained from the solution spectrum at 230 K ($A_{\perp}$ *ca.* 0 G). The solid-state spectrum of **13**$^{\cdot+}$ shows also some resolution, but not sufficient to give clear results. For **10**$^{\cdot+}$–**13**$^{\cdot+}$ there is considerable spin-density on the 2,5-substituents, with N > S > O as expected for radical cations.

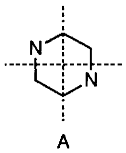
For the NR_2-substituted derivatives **12**$^{\cdot+}$ and **13**$^{\cdot+}$ it was possible to record resolved liquid-phase EPR spectra. These radical cations were generated from the parent pyrazines by electron transfer to tris(4-bromophenyl)aminium hexachloroantimonate (TBPA) in ethanol–dichloromethane (9 : 1). The EPR spectra (example given in Fig. 3) are well-simulated (values provided in Table 2) and give no evidence of hyperfine splittings of the ring nitrogens. ENDOR measurements unambiguously confirm the proton coupling constants of these radical cations. The EPR spectra in fluid solution show large hyperfine coupling constants for the two amino nitrogens (N^{α}) and the γ-protons. The spectra of **12**$^{\cdot+}$ and **13**$^{\cdot+}$ display two sets of NCH_3 and NCH_2 proton splittings in agreement with a restricted rotation of the amino substituents about the N–aryl bond, similar to that found in arylamine radical cations.[20] The observation that the H(γ) hyperfine coupling constant of the pyrrolidine derivative **13**$^{\cdot+}$ is larger than that of the dimethylamino compound **12**$^{\cdot+}$ is related to the dihedral angle θ between the nitrogen π-orbital and the β-hydrogen–carbon bond. The ring protons show remarkably large coupling constants, $a(H^{3,6})$ *ca.* 4 G. On the other hand, hyperfine splittings of the ring nitrogens could not be detected, indicating that the SOMO has nodes on the 1,4-nitrogens. These results show that **12**$^{\cdot+}$ and **13**$^{\cdot+}$ have a π-SOMO predominantly localised on the two exocyclic nitrogen atoms and on the 3,6-ring carbons.

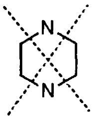
Radical Anions.—These were generated in the solid-state by exposing dilute solutions of **1**–**13** in CD_3OD at 77 K to ^{60}Co γ-rays. All EPR spectra are remarkably similar with parallel features of two equivalent ^{14}N nuclei flanking the intense solvent line corresponding to $A_{\parallel}$ *ca.* 19 G (Table 3). $A_{\perp}$ is mixed up with other small splittings. Using the isotropic data listed in Table 4, we calculate that $A_{\perp}$ must be small (*ca.* ±2 G). This shows conclusively that the radical anions are indeed as expected π* radical anions. In **1**$^{\cdot-}$ the estimated 2p character is *ca.* 37% on each nitrogen giving a total spin-density of *ca.* 74% on nitrogen. Considering $a(H^{2,3,5,6}) = -2.72$ G[21] ($Q_{CH} = -27$ G[22]), the total spin density in **1**$^{\cdot-}$ adds up to *ca.* 1.14 which is close to one, as expected. The deviation from unity is connected with the margin of error of the relationships applied.

Exhaustive EPR and ENDOR studies of **1**$^{\cdot-}$ in fluid solution yielded all ^1H, ^{14}N and ^{13}C hyperfine coupling constants, including their signs.[14,21] **1**$^{\cdot-}$ has also been the object of many calculations, *e.g.* HMO,[23] INDO,[21] *ab initio*.[24,25] Liquid phase EPR spectra of **4**$^{\cdot-}$, **6**$^{\cdot-}$, **8**$^{\cdot-}$ and **9**$^{\cdot-}$ have been observed prior to our investigations and their data are listed in Table 4 for comparison. **5**$^{\cdot-}$, **7**$^{\cdot-}$, **10**$^{\cdot-}$, **12**$^{\cdot-}$ and **13**$^{\cdot-}$ were generated by reduction of the parent pyrazines with potassium metal in 1,2-dimethoxyethane. The resolved EPR spectra are well simulated with the data given in Table 4. Only in case of **12**$^{\cdot-}$ a resolved potassium splitting, a(K) = 0.39 G, was observed (Fig. 4). All radical anions, **1**$^{\cdot-}$–**13**$^{\cdot-}$, yield large nitrogen coupling constants in the range 6–7 G.

Radical anions of benzene derivatives usually show considerable mixing of the two π-orbitals A and S which are degenerate for the symmetrical benzene radical anion. The ^{14}N and ^1H hyperfine coupling constants of the radical anions derived from pyrazine and its methyl substituted derivatives **1**$^{\cdot-}$–**9**$^{\cdot-}$ indicate a π-SOMO with predominant S-type character. Strong electron donor substituents, however, change the picture. The remarkable increase of $a(H^{3,6})$ in **10**$^{\cdot-}$, **12**$^{\cdot-}$ and

13$^{\bullet-}$ suggests that OCH_3 and NR_2 substituents in positions 2 and 5 convert the SOMO to an orbital with considerable A-type character. The same can be expected for the SCH_3 derivative. Unfortunately we were not able to observe **11**$^{\bullet-}$ in fluid solution.


A


S

Experimental

^{1}H NMR spectra of $CDCl_3$ solutions at room temperature were obtained with a Bruker HX-360 MHz instrument with tetramethylsilane as internal standard. Mass spectra were taken on a Dupont CEC 21-492 (70 eV).

For freon studies, very dilute solutions in $CFCl_3$ ($\leq 1:1000$) were deoxygenated, and frozen as small beads in liquid nitrogen. The freon was purified by passage through an alumina column. For solid alcohol studies, dilute solutions (*ca.* 1:100) were prepared in CD_3OD with low concentrations of D_2O or methyltetrahydrofuran to provide good glasses. Results were similar in both glass compositions.

Solutions were irradiated at 77 K in a ^{60}Co Vickrad γ-ray source for doses of a few hundred rad. EPR spectra of these irradiated samples were measured on a Varian E-109 spectrometer at 77 K. Samples were annealed by decanting the coolant from the insert Dewar flask, and allowing the sample to warm while continuously monitoring the spectra. Samples were recooled to 77 K for measurement. For studies at higher temperatures a Varian variable-temperature accessory was used.

EPR and ENDOR resonance spectra of the radical ions in the liquid-phase were measured with a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; *g*-values were determined with an NMR gaussmeter and the Hewlett-Packard frequency converter 5246 L, calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = (0.7145/*g*) G.

Table 3 ^{14}N Hyperfine coupling constants together with approximate orbital populations (%) on each nitrogen for the pyrazine radical anions **1**$^{\bullet-}$–**9**$^{\bullet-}$ in CD_3OD at 77 K

	$A_\parallel$/G	$A_\perp$/G	A_{iso}/G	$2B$	$a_p{}^2$ [a]
1$^{\bullet-}$	19.5	0 ± 2	7.2 [b]	12.3	37
2$^{\bullet-}$, **3**$^{\bullet-}$	19.0	0 ± 2	6.3	12.7	38
4$^{\bullet-}$, **5**$^{\bullet-}$	18.0	0 ± 2	6.7 [b]	11.3	34
6$^{\bullet-}$, **7**$^{\bullet-}$	19.0	0 ± 2	6.7 [b]	12.3	37
8$^{\bullet-}$	*c*	0 ± 2	7.4, 6.2 [b]		
9$^{\bullet-}$	19.0	0 ± 2	6.2 [b]	12.8	39

[a] The estimated 2s populations of *ca.* 1% have no direct structural significance. [b] Liquid-phase result. [c] Parallel features poorly defined.

Pyrazine **1** and the methyl substituted derivatives **2**, **4**, **6**, **8** and **9**, obtained commercially, were purified by distillation and **9** by additional zone melting. Deuteriation of the methyl groups in **2**, **4** and **6** was accomplished by H/D exchange in $NaOD/D_2O$.[26] **11** and **13** were prepared as described in the literature.[27] **10** and **12** were synthesised following known methods.[27,28]

General Procedure for Deuteriation.—(Yields were generally 70–84% and deuteriation *ca.* 98%.) 2-[$^2H_3$]*Methylpyrazine* **3**. Sodium (100 mg, 4.3 mmol) was dissolved in D_2O (20 cm^3) under nitrogen. After addition of 2-methylpyrazine **2** (2.35 g, 25 mmol) the solution was sealed in an ampoule and heated at 150 °C for 1 day. After cooling, the solution was extracted with diethyl ether (5 × 30 cm^3). The combined extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. This exchange procedure was repeated two times. The obtained deuteriated compound was distilled using a Fischer Micro-Spaltrohr-Column: **3** (1.8 g, 74%), b.p. 134–135 °C; δ_H 2.54 (0.04 H, m, CH_3), 8.38 (1 H, m, 3-H), 8.46 (2 H, m, 5,6-H); *m/z* 99 (6%), 98 (28), 97 (M^+, 100), 96 ($M^+ - 1$, 16), 95 ($M^+ - 2$, 2).

2,3-*Di*[$^2H_3$]*methylpyrazine* **5**. B.p. 155–156 °C; δ_H 2.51 (0.04 H, m, CH_3), 8.28 (2 H, s, 5,6-H); *m/z* 115 (8%), 114 (M^+, 100), 113 ($M^+ - 1$, 6).

2,5-*Di*[$^2H_3$]*methylpyrazine* **7**. B.p. 154–155 °C; δ_H 2.49 (0.06 H, m, CH_3), 8.34 (2 H, s, 3,6-H); *m/z* 116 (2%), 115 (21), 114 (M^+, 100), 113 ($M^+ - 1$, 8), 112 ($M^+ - 2$, 3).

2,5-*Dimethoxy*-3,6-*dihydropyrazine.*—A stirred mixture of piperazine-2,5-dione (11.4 g, 0.1 mol) and freshly prepared trimethyloxonium tetrafluoroborate[29] (37 g, 0.25 mol) in anhydrous dichloromethane was heated at reflux for 4 days. After the reaction mixture cooled, aqueous $NaHCO_3$ (1 mol dm^{-3}, 220 cm^3) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (4 × 100 cm^3). The combined organic layers were dried over $MgSO_4$. The solvent was removed by distillation and the obtained residue purified by fractional recrystallisation from light petroleum (b.p. 50–75 °C) to yield two products: 5-*methoxy*-3,6-*dihydropyrazine*-2(1H)-*one*, colourless crystals (0.20 g, 1.6%) from ethyl acetate–pentane, m.p. 180–181 °C (Found: C, 46.95; H, 6.4; N, 21.75. $C_5H_8N_2O_2$ requires: C, 46.87; H, 6.29; N, 21.86%); δ_H 3.72 (3 H, s, CH_3), 4.01 (2 H, dt, $^3J_{1\text{-H},6\text{-H}}$ 1.8 Hz,

Table 4 Isotropic hyperfine coupling constants for the pyrazine radical anions **5**$^{\bullet-}$, **7**$^{\bullet-}$, **10**$^{\bullet-}$, **12**$^{\bullet-}$ and **13**$^{\bullet-}$ in DME (reduction with potassium) at 300 K (EPR), together with literature EPR data for **1**$^{\bullet-}$,[21] **4**$^{\bullet-}$,[15] **6**$^{\bullet-}$,[16] **8**$^{\bullet-}$ [16] and **9**$^{\bullet-}$ [17,18]

	$a(N^{1,4})$/G	$a(H^2)$/G	$a(H^3)$/G	$a(H^5)$/G	$a(H^6)$/G	a(i)/G	g
1$^{\bullet-}$ [a]	+7.24	−2.72	−2.72	−2.72	−2.72	2.90 (^{13}C)	2.0036
4$^{\bullet-}$ [b]	6.66	1.76 [c]	1.76 [c]	2.43	2.43		2.0035
5$^{\bullet-}$	6.68	0.27 [d]	0.27 [d]	2.48	2.48		2.0035
6$^{\bullet-}$	6.67	1.13 [c]	3.46	1.13 [c]	3.46		2.0035
7$^{\bullet-}$	6.55		3.65		3.65		2.0035
8$^{\bullet-}$	6.16 (N^1) 7.35 (N^4)	2.04 [c]	2.85	2.85	2.04 [c]		2.0036
9$^{\bullet-}$	6.18	1.73 [c]	1.73 [c]	1.73 [c]	1.73 [c]	0.31 (1 K)	2.00355 [e]
10$^{\bullet-}$	5.88		6.37		6.37		2.0035
12$^{\bullet-}$	5.79		6.18		6.18	0.39 (2 N) 0.39 (1 K)	2.0035
13$^{\bullet-}$	5.90		5.90		5.90	0.40 (2 N)	2.0035

[a] Reduction with sodium in liquid ammonia at 223 K.[21] [b] Reduction with sodium in tetrahydrofuran.[15] [c] 3 H (CH_3). [d] 3 D (CD_3). [e] Ref. 18.

^5J 2.8 Hz, 6,6-H), 4.14 (2 H, t, 3,3-H), 6.57 (1 H, br. s, NH); *m*/*z* 128 (M^+, 100%).

2,5-*Dimethoxy*-3,6-*dihydropyrazine*, colourless crystals (8.0 g, 56%) from light petroleum (b.p. 50–75 °C), m.p. 57–58 °C (Found: C, 50.6; H, 7.3; N, 19.6. $C_6H_{10}N_2O_2$ requires C, 50.69; H, 7.09; N, 19.71%); δ_H 3.71 (6 H, s, CH_3), 4.05 (4 H, s, 3,3,6,6-H); *m*/*z* 142 (M^+, 100%).

2,5-*Dimethoxypyrazine* **10**.[30]—The combined solutions of 2,5-dimethoxy-3,6-dihydropyrazine (2.84 g, 20 mmol) in toluene (30 cm^3) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4.80 g, 21 mmol) in toluene (30 cm^3) were heated at reflux for 2 h. Column chromatography (silica gel, dichloromethane) afforded **10** (R_f: 0.57; 1.20 g, 43%) colourless crystals from pentane, m.p. 57–58 °C (Found: C, 51.2; H, 5.85; N, 20.0. $C_6H_8N_2O_2$ requires C, 51.42; H, 5.75; N, 19.99%); δ_H 3.92 (6 H, s, CH_3), 7.78 (2 H, s, 3,6-H); *m*/*z* 140 (M^+, 100%).

2,5-*Bis*(*dimethylamino*)3,6-*dihydropyrazine*.—Dimethylamine (22.5 g, 0.5 mol) was condensed at −78 °C into an ampoule, containing 2,5-diethoxy-3,6-dihydropyrazine[28] (8.50 g, 50 mmol). After sealing, the ampoule was heated at 60 °C for 6 h. The ampoule was cooled to −20 °C and opened, and the unreacted dimethylamine was allowed to evaporate at room temperature. Crystallisation of the residue from pentane afforded the product as colourless crystals (6.50 g, 77%), m.p. 95–96 °C (Found: C, 57.35; H, 9.5; N, 33.75. $C_8H_{16}N_4$ requires C, 57.11; H, 9.59; N, 33.30%); δ_H 2.94 (12 H, s, CH_3), 4.16 (4 H, s, 3,3,6,6-H); *m*/*z* 168 (M^+, 100%).

2,5-*Bis*(*dimethylamino*)*pyrazine* **12**.—The combined solutions of 2,5-bis(dimethylamino)-3,5-dihydropyrazine (4.20 g, 25 mmol) in toluene (60 cm^3) and tetrachloro-1,4-benzoquinone (6.20 g, 25.2 mmol) in toluene (60 cm^3) were stirred and heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was treated with aqueous NaOH (2 mol dm^{-3}, 60 cm^3). The mixture was extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography of the residue [silica gel, dichloromethane–ethyl acetate (2:1)] afforded **12** (R_f: 0.6, 2.60 g, 63%) yellow fluorescent crystals from pentane, m.p. 87–88 °C (Found: C, 57.8; H, 8.7; N, 33.85. $C_8H_{14}N_4$ requires C, 57.80; H, 8.49; N, 33.71%); δ_H 2.99 (12 H, s, CH_3), 7.70 (2 H, s, 3,6-H); *m*/*z* 166 (M^+, 100%).

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft.

References

1 D. N. R. Rao, G. W. Eastland and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2803.

2 H. Fischer, I. Umminger, F. A. Neugebauer, H. Chandra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1986, 837; H. Fischer, T. Müller, I. Umminger, F. A. Neugebauer, H. Chandra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1988, 413.

3 H. Fischer, F. A. Neugebauer, H. Chandra and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1989, 727.

4 (*a*) T. Kato and T. Shida, *J. Am. Chem. Soc.*, 1979, **101**, 6869; (*b*) M. Matsushita, T. Momose, T. Kato and T. Shida, *Chem. Phys. Lett.*, 1989, **161**, 461.

5 T. Shida and T. Kato, *Chem. Phys. Lett.*, 1979, **68**, 106.

6 M. C. R. Symons and I. G. Smith, *J. Chem. Res. (S)*, 1979, 382.

7 K. Toriyama, K. Nunome and M. Iwasaki, *J. Phys. Chem.*, 1981, **85**, 2149.

8 J. T. Wang and F. Williams, *Chem. Phys. Lett.*, 1981, **82**, 177.

9 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.

10 R. Gleiter, E. Heilbronner and V. Hornung, *Helv. Chim. Acta*, 1972, **55**, 255; K. A. Muszkat and J. Schäublin, *Chem. Phys. Letters*, 1972, **13**, 301.

11 E. Haselbach, Z. Lanyiova and M. Rossi, *Helv. Chim. Acta*, 1973, **56**, 2889.

12 P. Bischof, R. Gleiter and P. Hofmann, *J. Chem. Soc., Chem. Commun.*, 1974, 767.

13 D. N. R. Rao, G. W. Eastland and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 727.

14 *Magnetic Properties of Free Radicals, Landolt–Börnstein*, Springer, Berlin, Heidelberg, New York, New Series, Group II, 1965, **1**, 115; 1980, **9d1**, 870–871, 1988, **17f**, 199–200.

15 W. Kaim, *J. Organomet. Chem.*, 1981, **215**, 337.

16 C. A. McDowell and K. F. G. Paulus, *Mol. Phys.*, 1964, **7**, 541.

17 C. A. McDowell and K. F. G. Paulus, *Can. J. Chem.*, 1965, **43**, 224.

18 C. Carre, J. Courtieu, J. Jullien and H. Stahl-Lariviere, *Spectrochim. Acta, Part A*, 1986, **42**, 1201.

19 M. C. R. Symons, *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*, Van Nostrand Reinhold Co. Ltd., Wokingham, Berkshire, England, 1978.

20 F. A. Neugebauer, H. Fischer and H. Weger, *Chem. Ber.*, 1977, **110**, 2802; K. Elbl-Weiser, F. A. Neugebauer and H. A. Staab, *Tetrahedron Lett.*, 1989, **30**, 6161.

21 W. Lubitz and T. Nyrönen, *J. Magn. Res.*, 1980, **41**, 17.

22 H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632, 764; E. T. Strom, G. R. Underwood and D. Jurkowitz, *Mol. Phys.*, 1972, **24**, 901.

23 A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 21.

24 A. Hinchliffe, *Int. J. Quant. Chem.*, 1977, **11**, 767.

25 M. H. Palmer and I. Simpson, *Z. Naturforsch., A*, 1983, **38**, 415.

26 T. W. S. Lee and R. Stewart, *Can. J. Chem.*, 1986, **64**, 1085.

27 R. Gompper and W. Breitschaft, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 717; *Angew. Chem.*, 1983, **95**, 727. W. Breitschaft, Dissertation, Ludwig-Maximilian-Universität, München, 1984.

28 K. W. Blake, A. E. A. Porter and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2494; J. L. Markham and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1889.

29 H. Meerwein, *Org. Synth.*, Coll. Vol. V, 1080, 1096.

30 This compound [δ_H 3.90 (6 H, s, CH_3), 7.75 (2 H, s, 3,6-H)] has already been reported by I. M. Dawson, J. A. Gregory, R. B. Herbert and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2585.

Paper 1/04582B
Received 4*th September* 1991
Accepted 8*th October* 1991