Radical Ions of [2.2](2,5)Pyrazinophanes: An Electron Paramagnetic Resonance Study

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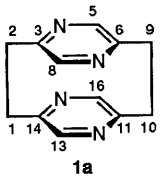
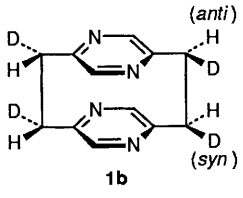
In the *pseudo-geminal* (**1a**) and *pseudo-ortho* [2.2](2,5)pyrazinophane (**2a**) the methylene hydrogens oriented *syn* towards the aza function can be selectively replaced by deuterium, to give **1b** and **2b**. The corresponding radical anions were generated in 1,2-dimethoxyethane by reaction of the parent compounds with alkali metal mirror, and their EPR and ENDOR spectra were recorded. General triple resonance, providing the relative signs of the ^1H coupling constants, and selective deuteriation of the *syn* methylene hydrogens led to full assignment in all cases. As anticipated, the magnitudes of the nitrogen and ring proton coupling constants are about one half the magnitudes of those of the corresponding 2,5-dimethylpyrazine radical anion **3**$^{\bullet-}$. For the two sets of methylene protons, considerably different coupling constants were found; **1a**$^{\bullet-}$: $a(H_{syn})$ = +2.54, $a(H_{anti})$ = +0.24 G; **2a**$^{\bullet-}$: $a(H_{syn})$ = +1.60, $a(H_{anti})$ = +0.30 G. The radical cations of **1a** and **2a** were prepared by exposure of the parent compounds, as dilute solutions in $CFCl_3$, to ^{60}Co γ-rays at 77 K. The results establish that these are π-radicals rather than σ-radicals despite the fact that the dimethylated monomers (pyrazine radical cations) are clearly σ-species. The results for the *pseudo-ortho*-derivative cation show that there are two sets of inequivalent CH_2 protons.

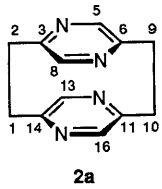
In the last three decades radical ions of numerous carbocyclophanes have been the subject of extensive EPR and ENDOR studies which have revealed detailed information on their structure, spin density distribution, ion pair formation, and reactivity.[1–9] Much less, however, is known about heterocyclophane radical ions. To our knowledge, there is only one report mentioning azacyclophane radical ions, namely radical anions derived from *pseudo-ortho* and *pseudo-para* [2.2](2,5)pyridinophanes (two of four possible isomers) and [2]*para*cyclo[2](2,5)pyridinophane.[10] The EPR spectra of these species, however, were only poorly resolved and require further study. Motivated by our interest in the properties of azacyclophanes we recently synthesized both [2.2](2,5)pyrazinophanes, the *pseudo-geminal* **1a** and the *pseudo-ortho* isomer **2a**, and



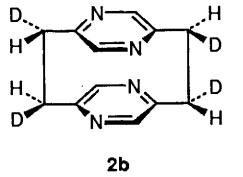
1a



1b



2a



2b

established their structural assignment unequivocally by X-ray structure determinations.[11] We report here that **1a** and **2a**, as solutions in 1,2-dimethoxyethane (DME), can be reduced with alkali metal to generate the corresponding radical anions **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$. Furthermore, when solutions of **1a** and **2a** in $CFCl_3$ at 77 K were exposed to ^{60}Co γ-rays, and then annealed, EPR spectra were observed which we assign to the radical cations **1a**$^{\bullet+}$ and **2a**$^{\bullet+}$. In the analysis of the EPR spectra of these radical ions one must take into account that there are three sets of four equivalent hydrogens, since the hydrogens of the methylene groups are inequivalent, as well as the set of four equivalent nitrogens. Our assignment of the ^1H coupling constants is based on selective deuteriation and the results of general triple resonance experiments.[12]

Results and Discussion

Selective Deuteriation of **1a** *and* **2a**.—In a number of heterocyclic systems, including pyrazine, hydrogens of methyl groups conjugated to aza or azonium functions are acidic and can be selectively replaced by deuterium.[13,14] Therefore, it seemed possible that in azacyclophanes, such as our [2.2](2,5)-pyrazinophanes, the ethylene bridges would incorporate deuterium faster than the pyrazine rings. H. A. Staab and M. Decker[15] observed during NMR studies of *pseudo-meta* and *pseudo-geminal* 5,14-bis(methoxycarbonyl)[2.2.2](1,2,6)-pyridiniophane dibromides that, on standing in D_2O for two days, the four inner hydrogens of the 1,6-ethylene bridges were stereoselectively replaced by deuterium. Our NaOD/D_2O exchange experiments with the [2.2](2,5)pyrazinophanes **1a** and **2a** show that the methylene hydrogens oriented *syn* towards the aza function in these compounds undergo deuterium exchange faster than those oriented *anti*. Since the exchange is rather slow, stronger experimental conditions had to be applied. Furthermore, the extent of deuteriation had to be stopped at an optimal level, since the *anti* methylene hydrogens also underwent a slower exchange process. NMR measurements (Fig. 1) in combination with mass spectra indicated that under our experimental conditions the deuteriation of the *syn* methylene hydrogens in **1b** and **2b** was almost complete, with an additional 5–30% deuterium incorporation in the *anti* positions.

Radical Anions **1a**$^{\bullet-}$, **1b**$^{\bullet-}$, **2a**$^{\bullet-}$ *and* **2b**$^{\bullet-}$.—In 1,2-dimethoxyethane **1a**, **1b**, **2a** and **2b** reacted with alkali metal to generate the corresponding radical anions which were sufficiently long-lived to be studied by EPR and ENDOR spectroscopy. The form-

Table 1 Isotropic hyperfine coupling constants for the radical anions $\mathbf{1a}^{\bullet -}$, $\mathbf{1b}^{\bullet -}$, $\mathbf{2a}^{\bullet -}$, $\mathbf{2b}^{\bullet -}$ and $\mathbf{3}^{\bullet -}$ in 1,2-dimethoxyethane (DME)

	Method	a(N)/G	a(H^{α})/G	a(*syn*-H^{β})/G	a(*anti*-H^{β})/G	g
$\mathbf{1a}^{\bullet -}$	EPR[a]	2.97 (4N)	2.47 (4 H)	2.47 (4 H)	0.30 (4 H)	2.0038
$\mathbf{1a}^{\bullet -}$	ENDOR[b]		−2.54	+2.54	+0.24	
$\mathbf{1b}^{\bullet -}$	ENDOR[b]		−2.54		+0.24	
$\mathbf{2a}^{\bullet -}$	EPR[c]	3.18 (4N)	2.15 (4 H)	1.59 (4 H)	0.28 (4 H)	2.0037
$\mathbf{2a}^{\bullet -}$	ENDOR[d]		−2.15	+1.60	+0.30	
$\mathbf{2b}^{\bullet -}$	ENDOR[d]		−2.15		+0.30	
$\mathbf{3}^{\bullet -}$	EPR[e]	6.67 (2N)	(−)3.46 (2 H)	(+)1.13 (6 H, CH_3)		2.0035

[a] Reduction with sodium at 300 K. [b] Reduction with sodium at 230 K. [c] Reduction with potassium at 250 K. [d] Reduction with potassium at 230 K. [e] Reduction with potassium at 300 K.[16]

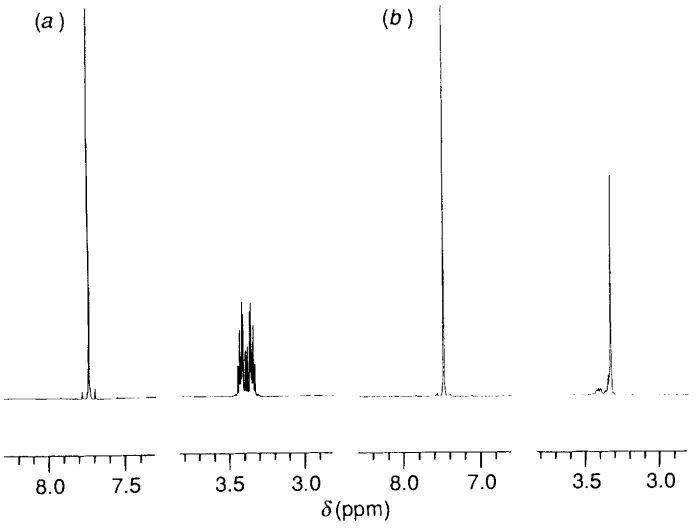


Fig. 1 ^{1}H NMR spectra of *pseudo-geminal* [2.2](2,5)pyrazinophane **1a** (*a*) and *pseudo-geminal* (1*R*),(2*S*),(9*S*),(10*R*)[$^2H_4$][2.2](2,5)pyrazinophane **1b** (*b*) in $CDCl_3$

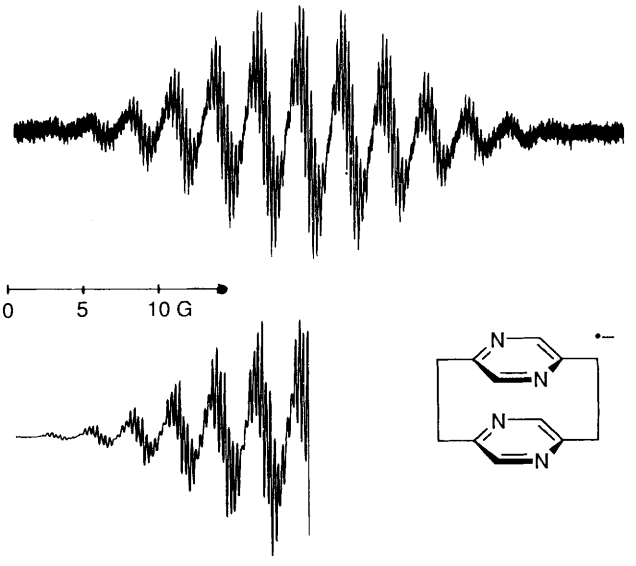
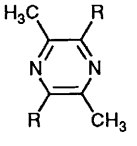


Fig. 2 First derivative X-band EPR spectrum for the radical anion of *pseudo-geminal* [2.2](2,5)pyrazinophane $\mathbf{1a}^{\bullet -}$ in DME at 300 K together with a simulation using the data in Table 1

ation of the radical anions, however, depended considerably on the experimental conditions, namely on the reducing agent, the reaction time, and the temperature. Frequently we obtained mixtures of the desired radical anion and other secondary paramagnetic species. Assuming that the unpaired electron interacts with all ^{1}H and ^{14}N nuclei, for $\mathbf{1a}^{\bullet -}$ and $\mathbf{2a}^{\bullet -}$ one would expect isotropic hyperfine coupling constants arising from one set of four equivalent nitrogens and three sets of four equivalent hydrogens, these being the ring protons and the *syn* and *anti* methylene protons. Furthermore, the EPR data of the 2,5-dimethylpyrazine radical $\mathbf{3}^{\bullet -}$[16] (Table 1) predict that the [2.2](2,5)pyrazinophane radical anions will display a nitrogen coupling constant in the range of +3 G, a ring proton splitting of *ca.* −2 G, and positive signs for the methylene proton splittings. As expected, the *g*-values of $\mathbf{1a}^{\bullet -}$: 2.0038, and $\mathbf{2a}^{\bullet -}$: 2.0037, are close to that of $\mathbf{3}^{\bullet -}$: 2.0035.



3; R = H
4; R = CH_3

Fig. 2 shows a highly resolved EPR spectrum of $\mathbf{1a}^{\bullet -}$ obtained by reaction of **1a** with a sodium mirror at 300 K, together with a simulation using the following hyperfine coupling constants: 2.97 (4N), 2.47 (8 H) and 0.30 G (4 H). This analysis is supported by the ^{1}H ENDOR spectrum of $\mathbf{1a}^{\bullet -}$ at 230 K which shows only two pairs of signals corresponding to coupling constants of 2.54 and 0.24 G. Apparently, two proton sets have similar coupling constants. There are two alternative explanations, one being that one set of β protons has a large coupling (+2.54 G), equal to the ring proton coupling (−2.54 G) and the other set of β protons has a small coupling (±0.24 G). The other interpretation is that the 8 β protons are effectively equivalent at this temperature. Since the latter view gives unacceptable small magnitudes for the ring protons, we favour the former. Further studies supported our supposition. General triple resonance experiments did not affect the relative intensities of the ENDOR signals of $\mathbf{1a}^{\bullet -}$, indicating that the two sets of equivalent protons (2.54 G) have opposite signs. The ^{1}H ENDOR spectrum of the deuteriated derivative $\mathbf{1b}^{\bullet -}$ again shows two signal pairs with splittings of 2.54 and 0.24 G, respectively. However, for this compound general triple resonance affected the intensities of the ENDOR signals. The sign of the 2.54 G coupling constant is opposed to that of 0.24 G. By comparing the EPR and ENDOR results for $\mathbf{1a}^{\bullet -}$ and $\mathbf{1b}^{\bullet -}$ with those of the reference radical anion $\mathbf{3}^{\bullet -}$, a clear assignment of all hyperfine coupling constants can be made. We attribute a negative sign to one set of the 2.54 G coupling constant of $\mathbf{1b}^{\bullet -}$ and assign this splitting to the ring protons. Consequently, the remaining proton coupling constants are positive. The large splitting of +2.54 G clearly belongs to the *syn*, the small splitting of +0.24 G to the *anti* methylene protons.

For $\mathbf{2a}^{\bullet -}$ a highly resolved EPR spectrum (Fig. 3) was obtained by reduction of **2a** with a potassium mirror at 250 K. Its simulation was computed using the hyperfine coupling constants given in Table 1. The ^{1}H values were affirmed by the

corresponding ^{1}H ENDOR spectrum displayed in Fig. 4, which also shows the effect of a general triple resonance experiment on the intensities of the ENDOR signals. Accordingly, the sign of 2.15 G coupling constant is opposite to those of the 1.60 and 0.30 G splittings. ^{1}H ENDOR of the deuteriated derivative **2b**$^{\bullet -}$ shows only two clear signal pairs, the 2.15 and 0.30 G splittings, which again are opposed in their signals. By comparing the EPR and particularly the ^{1}H ENDOR spectra of **2a**$^{\bullet -}$ and **2b**$^{\bullet -}$ an unambigious assignment of all coupling constants, as listed in Table 1, can be made.

As predicted, the magnitudes of the nitrogen and ring proton coupling constants of **1a**$^{\bullet -}$ and **2a**$^{\bullet -}$ are about one half the magnitudes of the corresponding values for **3**$^{\bullet -}$. Unexpectedly, however, the coupling constants of the *syn* and *anti* methylene protons differ significantly. The hyperfine interaction of protons in a position β to a π-centre usually follows the $\cos^2\theta$ relationship: $a(\mathrm{H}) = B_0 + B(\cos^2\theta)\rho_C$,[17] indicating that the different values for the *syn* and *anti* methylene proton splittings may be related to different torsional angles, θ, defined by the $2p_z$ axis at the π-centre and the direction of the corresponding β C–H bond. Different θ angles for the methylene protons could be caused by a slight lateral shift of the pyrazine rings relative to each other and parallel to the ring plane. With this in mind, one would expect that the *pseudo-geminal* isomer **1a**$^{\bullet -}$ would have slightly different θ angles for the *syn* and the *anti* methylene protons. However, this explanation does not apply to the *pseudo-ortho* isomer **2a**$^{\bullet -}$. Such a lateral shift for this compound always results in the two *syn* and two *anti* C–H bonds having the same θ angle. This is incompatible with our results. Thus we speculate that the considerable difference between the methylene proton splittings must be connected with electronic interactions, *i.e.* through-bond and/or through-space interactions induced by the ring nitrogens. Comparable effects were observed for a carbocyclophane with four ethylene bridges, *i.e.* for the [2$_4$](1,2,4,5)cyclophane radical anion.[18] The EPR and ENDOR study of this radical anion also yielded two significantly different coupling constants for the methylene protons which were assigned on the basis of INDO calculations: $a(\mathrm{H}_{exo}) = 2.45$ (8 H) and $a(\mathrm{H}_{endo}) = 0.33$ G (H_{endo}, which is the methylene hydrogen oriented to the adjacent ethylene bridge). The SOMO of the [2$_4$](1,2,4,5)cyclophane radical anion is thought to be a bonding combination of symmetric-like MOs of two benzene π-systems.[18] In **1a**$^{\bullet -}$ and **2a**$^{\bullet -}$, however, the observed coupling constants of the nitrogens (*a ca.* 3 G) and ring protons (*a ca.* 2.2 G) give evidence of comparable π-spin densities at the corresponding ring positions. The relative increase of $a(\mathrm{H}^a)$ from 3.46 G to *ca.* 4.4 G (two times *ca.* 2.2 G) indicates that the π-SOMO of the 2,5-dimethylpyrazine radical anion with predominant symmetric character is changed in the [2.2]cyclophane arrangement towards a π-SOMO with some antisymmetric character.[19,20] INDO calculations failed to give further insight.

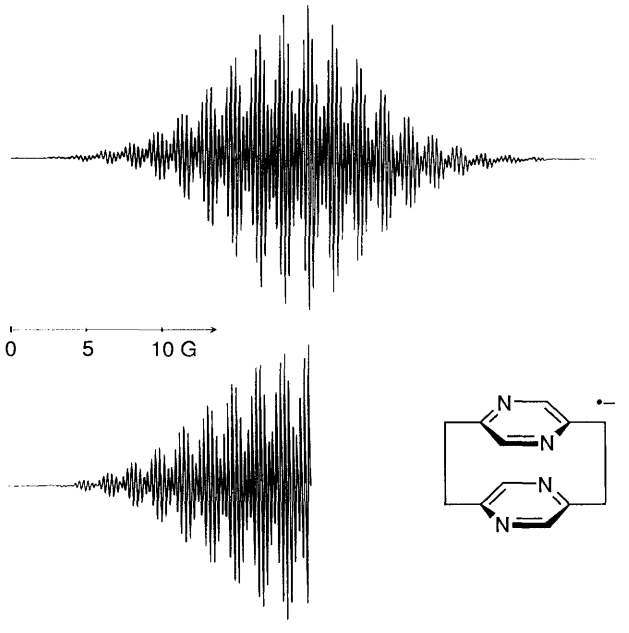


Fig. 3 First derivative X-band EPR spectrum for the radical anion of *pseudo-ortho* [2.2](2,5)pyrazinophane **2a**$^{\bullet -}$ in DME at 250 K together with a simulation using the data in Table 1

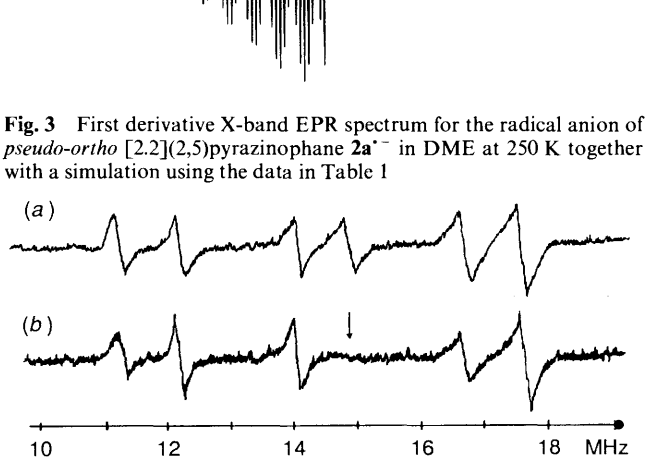


Fig. 4 ^{1}H ENDOR spectrum of the radical anion of *pseudo-ortho* [2.2](2,5)pyrazinophane **2a**$^{\bullet -}$ in DME at 210 K (*a*) together with the general triple resonance spectrum, pump frequency 14.88 MHz (*b*)

Radical Cations **1a**$^{\bullet +}$, **1b**$^{\bullet +}$, **2a**$^{\bullet +}$ *and* **2b**$^{\bullet +}$.—Recent EPR studies of methylated pyrazine radical cations, readily generated by γ-irradiation of dilute solutions of the parent compounds in $CFCl_3$ at 77 K,[21] gave clear evidence of a reversal in the sequence of the two highest MOs.[20] In agreement with PES (photoelectron spectroscopy) results and calculations[22] the switch of the SOMO from n(σ) to π lies between the dimethyl derivative **3**$^{\bullet +}$ and the tetramethyl species **4**$^{\bullet +}$. Therefore, the SOMO of [2.2](2,5)pyrazinophane radical cations, which have the same substitution pattern as **3**, is expected to be close to this reversal in the wave function. EPR studies of **1a**$^{\bullet +}$ and **2a**$^{\bullet +}$ should reveal whether the π–π interaction between the pyrazine units in the cyclophanes is strong enough to shift the highest π orbital to a lower energy level than that of the first σ orbital.

The EPR results for $CFCl_3$ solutions clearly establish the formation of delocalized π-radical cations in preference to σ-radicals. For some reason only the *pseudo-ortho* radical cation **2a**$^{\bullet +}$ spectrum was resolved into proton hyperfine components, that for the *pseudo-geminal* cation **1a**$^{\bullet +}$ being a single broad line (ΔH_{MS} *ca.* 23 G). This width roughly corresponds to that for the former, when the lines are just too broad for resolution, so the hyperfine parameters are probably comparable. Our best simulation for the *pseudo-ortho* species gave $A(4\ \mathrm{H}) = 9$ G and $A(4\ \mathrm{H}) = 13$ G (Fig. 5). Thus again, the two sets of four protons are clearly differentiated.

For the species with four ^{1}H and four ^{2}H nuclei in the methylene groups, the *pseudo-ortho* **2b**$^{\bullet +}$ gave a set of five broad lines with $A(^1\mathrm{H})$ *ca.* 13 G. Based on this result we assign the larger splitting of *ca.* 13 G to the *anti*- and the smaller one of *ca.* 9 G to the *syn*-methylene protons. The partly deuteriated *pseudo-geminal* derivative **1b**$^{\bullet +}$ still gave a broad line with no clear resolution although ΔH_{MS} was reduced to *ca.* 14 G. The corresponding perdeuteriated species gave a relatively narrow singlet, ΔH_{MS} *ca.* 9 G. Unfortunately, hyperfine coupling to the ring protons and to ^{14}N still remained unresolved. We do not understand why the spectra for the *pseudo-ortho* radical cations are better resolved.

Noticeable is the large magnitude of the hyperfine coupling constants found for the methylene protons of **2a**$^{\bullet +}$. Their magnitude probably results from the well established positive charge effect[23] and indicates considerable σ–π delocalisation (hyperconjugation) from the C–H σ-orbitals into the ring π-system. For comparison, the EPR spectrum of the 1,4-dimethyl-

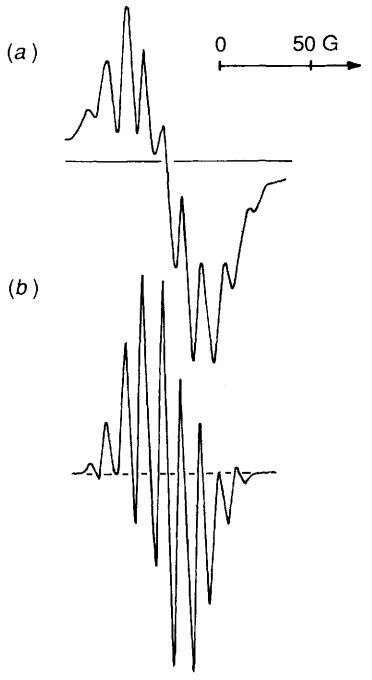


Fig. 5 (*a*) First derivative X-band EPR spectrum for a solution of *pseudo-ortho* [2.2](2,5)pyrazinophane **2a** in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K followed by annealing, showing features assigned to the corresponding radical cation $\mathbf{2a}^{\bullet+}$, together with a simulation using the data in text (*b*)

benzene radical cation displays a methyl proton splitting of 18.2 G.[23]

Experimental

^1H NMR spectra of $CDCl_3$ solutions at room temperature were obtained with a Bruker AM 500 MHz instrument with tetramethylsilane as internal standard. Mass spectra were taken on a Finnigan MAT 212 spectrometer (ionization energy 70 eV).

For the 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. 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.

EPR, ENDOR and general triple resonance spectra of the radical anions 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 counter 5342 A calibrated with the perylene radical cation. Hyperfine coupling constants measured in MHz (ENDOR) were converted into gauss using 1 MHz = (0.7145/*g*) G.

The *pseudo-geminal* (**1a**) and the *pseudo-ortho* [2.2](2,5)-pyrazinophane (**2a**) had been previously prepared in our laboratory.[11]

Pseudo-geminal(1R),(2S),(9S),(10R)[$^2H]_4$[2.2](2,5)*pyrazinophane* **1b**.—Sodium (150 mg, 6.5 mmol) was dissolved in a solution of ethan[$^2H_1$]ol (10 cm^3, 99.5%, Aldrich) in D_2O (10 cm^3, 99.75%, Merck) under nitrogen. After addition of powdered **1a** (212 mg, 1 mmol) the mixture was sealed in an ampoule and heated at 150 °C for 1 day. After cooling the mixture was extracted with trichloromethane (5 × 20 cm^3). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. This exchange procedure was repeated two or three times. The progress of deuteriation was checked by ^1H NMR spectroscopy. Recrystallization of the residue from ethyl acetate yielded colourless crystals (130 mg, 60%), m.p. 296–298 °C; δ_H 3.33 (s, *ca.* 4 H, 1,2,9,10-H, assignment confirmed by NOE), 7.74 (s, 4 H, 5,8,13,16-H); *m/z* 218 (19%), 217 (44), 216 (M^+, 100) and 215 (13).

Pseudo-ortho (1S),(2S),(9S),(10S)[$^2H_4$][2.2](2,5)*pyrazinophane* **2b**.—Prepared as described above using sodium (150 mg, 6.5 mmol), ethan[$^2H_1$]ol (10 cm^3, 99.5%, Aldrich), D_2O (10 cm^3, 99.75%, Merck) and **2a** (424 mg, 2 mmol). Recrystallization of the crude product from ethyl acetate gave colourless crystals (280 mg, 65%), m.p. 256–257 °C; δ_H 3.23 (s, *ca.* 4 H, 1,2,9,10-H, assignment confirmed by NOE) accompanied by multiplets of low intensity in the range 3.22–3.25 and 3.37–3.40, 7.81 (s, 4 H, 5,8,13,16-H); *m/z* 218 (67%), 217 (100), 216 (M^+, 93) and 215 (58).

Acknowledgements

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References

1 S. I. Weisman, *J. Am. Chem. Soc.*, 1958, **80**, 6462.
2 F. Gerson, *Top. Curr. Chem.*, 1983, **115**, 57.
3 A. de Meijere, F. Gerson, B. König, O. Reiser and T. Wellauer, *J. Am. Chem. Soc.*, 1990, **112**, 6827.
4 J. Bruhin, U. Buser, F. Gerson and T. Wellauer, *Helv. Chim. Acta*, 1990, **73**, 2058.
5 F. Gerson, W. Huber and T. Wellauer, *Helv. Chim. Acta*, 1989, **72**, 1428.
6 J. Bruhin, F. Gerson, W. B. Martin and H. Novotny, *J. Am. Chem. Soc.*, 1988, **110**, 6377.
7 F. Gerson, W. B. Martin, H. N. C. Wong and C. W. Chan, *Helv. Chim. Acta*, 1987, **70**, 79.
8 F. Gerson, R. Heckendorn, R. Möckel and F. Vögtle, *Helv. Chim. Acta*, 1985, **68**, 1923.
9 J. Bruhin, F. Gerson, R. Möckel and G. Plattner, *Helv. Chim. Acta*, 1985, **68**, 377.
10 F. Gerson, *Top. Curr. Chem.*, 1983, **115**, 92.
11 U. Eiermann, C. Krieger, F. A. Neugebauer and H. A. Staab, *Tetrahedron Lett.*, 1988, **29**, 3655; *Chem. Ber.*, 1990, **123**, 532.
12 H. Kurreck, B. Kirste and W. Lubitz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 173; *Angew Chem.*, 1984, **96**, 171.
13 T. W. S. Lee and R. Stewart, *Can. J. Chem.*, 1986, **64**, 1085, and literature cited therein.
14 A. T. Balaban, *J. Labelled Compd.*, 1981, **18**, 1621; A. T. Balaban, C. Uncata and F. Chiraleu, *J. Labelled Compd.*, 1982, **19**, 783; A. T. Balaban, M. D. Gheorghiu and T. S. Balaban, *J. Labelled Compd.*, 1983, **20**, 1097; A. T. Balaban, T. S. Balaban, C. Uncuta, M. D. Gheorghiu and F. Chiraleu, *J. Labelled Compd.*, 1983, **20**, 1105.
15 H. A. Staab and M. Decker, unpublished results; M. Decker, Dissertation, Universität Heidelberg, 1988.
16 C. A. McDowell and K. F. G. Paulus, *Mol. Phys.*, 1964, **7**, 541.
17 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.
18 F. Gerson, J. Lopez and V. Boeckelheide, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1298.
19 W. Lubitz and T. Nyrönen, *J. Magn. Reson.*, 1980, **41**, 17.
20 U. Eiermann, F. A. Neugebauer, H. Chandra, M. C. R. Symons and J. L. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, preceding paper.
21 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.
22 P. Bischof, R. Gleiter and P. Hofmann, *J. Chem. Soc., Chem. Commun.*, 1974, 767.
23 M. C. R. Symons and L. Harris, *J. Chem. Res. (S)*, 1982, 268.

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