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261. The Radical Anion of 2,7-Diazapyrene, a Change in Orbital Sequence on Protonation

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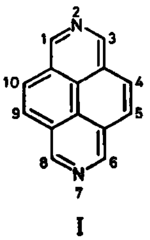
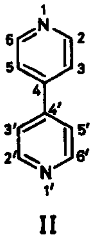
Summary. ESR.-spectra are reported for the radical anion $I\cdot^{\ominus}$ of 2,7-diazapyrene (I), along with those for the radical cations $I(2H)\cdot^{\oplus}$ and $I(2CH_3)\cdot^{\oplus}$ of 2,7-dihydro-2,7-diazapyrene and its 2,7-dimethyl-derivative, respectively. In contrast to the analogous radical ions of 4,4'-bipyridyl (II) and other previously studied diazaaromatic compounds, there is a striking change in the ^{14}N and proton coupling constants on going from the radical anion $I\cdot^{\ominus}$ to the radical cations $I(2H)\cdot^{\oplus}$ and $I(2CH_3)\cdot^{\oplus}$. This change can be rationalized in terms of the HMO model of the pyrene-π-system. A reversal in the energy sequence of the lowest antibonding orbitals is predicted upon an increase in the absolute value of the *Coulomb* integral for the azasubstituted π-centres, such an increase simulating the enhanced electronegativity of the azanitrogen atoms 2 and 7 on protonation.

Several azaaromatic compounds are known to form *diprotonated radical anions* when reduced chemically or electrolytically in acidic medium [1–5]. Such paramagnetic species bear an overall positive charge and will therefore be denoted in this paper as radical cations of the corresponding dihydroazaaromatic compounds or more briefly as *radical cations*. They have been thus far produced from compounds containing two azanitrogen atoms in 1,4-positions of one benzene ring (pyrazine, s-tetrazine, quinoxaline and phenazine) or in 4,4'-positions of a biphenyl π-system (4,4'-bipyridyl). If one ignores the further splittings from the two additional protons, the ESR.-spectra of the dihydro radical cations display hyperfine structures similar to those of the corresponding unprotonated radical anions. This result, which points to essentially the same nodal properties of the singly occupied orbitals, is not unexpected, since protonation of the azanitrogen lone pairs leaves the numbers of π-elec-



I

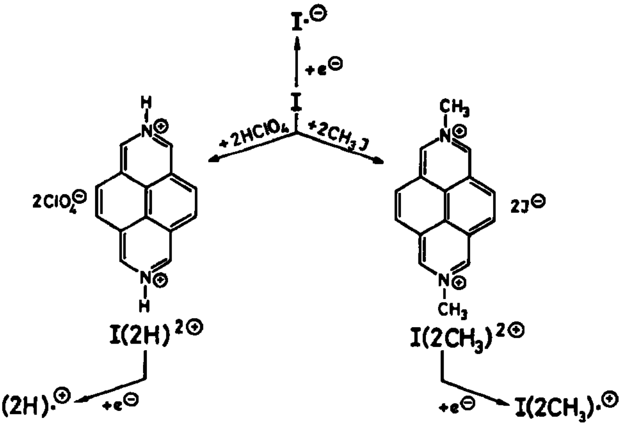


II

trons and π-centres unchanged, and its main effect is an increase in the electronegativity of the heteroatom involved. Although such an increase alters the orbital energies, the sequence of the levels in the relevant lowest antibonding region is preserved for all the azaaromatic π-systems mentioned above. That this situation need not be encountered in every case is demonstrated below.

In the present paper, ESR.-studies are reported of the radical ions produced from 2,7-diazapyrene (I). These ions comprise the radical anion $I^{\cdot\ominus}$, as well as the dihydro radical cation $I(2H)^{\cdot\oplus}$ and its N,N′-dimethyl-derivative $I(2CH_3)^{\cdot\oplus}$. The physico-chemical properties of $I(2CH_3)^{\cdot\oplus}$ have been previously studied by *Hünig et al.* [6]¹) who compared them with those of the well-known bipyridyl analogue $II(2CH_3)^{\cdot\oplus}$ [8].

Experimental Part. – 2,7-Diazapyrene (I) [9] was a generous gift of Prof. *W. Jenny*, Ciba-Geigy SA, Basel. Protonation of I in 70 percent perchloric acid converted it into $I(2H)^{2\oplus}2ClO_4^{\ominus}$, whereas its alkylation by methyl iodide led to $I(2CH_3)^{2\oplus}2J^{\ominus}$.



The radical anion $I\cdot^{\ominus}$ was produced by reaction of 2,7-diazapyrene (I) with potassium in 1,2-dimethoxyethane (DME). An analogous treatment of the dications $I(2H)^{2\oplus}$ and $I(2CH_3)^{2\oplus}$ with zinc in methanol or 80 percent acetic acid resulted in formation of the respective radical cations $I(2H)\cdot^{\oplus}$ and $I(2CH_3)\cdot^{\oplus}$. The stability of $I\cdot^{\ominus}$ and $I(2CH_3)\cdot^{\oplus}$ was much superior to that of $I(2H)\cdot^{\oplus}$. Thus the two former radical ions were also readily generated by an electrolytic reduction of I and $I(2CH_3)^{2\oplus}$, respectively, in N,N-dimethylformamide (DMF) with tetraethylammonium-perchlorate as supporting salt. On the other hand, no measurable concentration of $I(2H)\cdot^{\oplus}$ could be detected by ESR.-spectroscopy upon an electrolysis of $I(2H)^{2\oplus}$ under the same conditions. When the voltage was raised considerably above the value appropriate for such a reduction process [4], the ESR.-spectrum of the radical anion $I\cdot^{\ominus}$ appeared with a concommitant evolution of a gas in the sample tube. The obvious overall reaction $I(2H)^{2\oplus} + 3e^{\ominus} \rightarrow I\cdot^{\ominus} + H_2$ could not be prevented by the presence of small amounts of perchloric acid added to the solution of $I(2H)^{2\oplus}$ in DMF.

Results. – *Radical Anion* $I^{\cdot\ominus}$. The ESR.-spectrum of $I\cdot^{\ominus}$ in DME (counter-ion: $K^{\oplus}$) is shown in Fig. 1. Its relatively simple hyperfine pattern arises from the coupling constants (in Gauss²))

$$a_{N2,7} = 1.57 \pm 0.01;\ a_{H1,3,6,8} = 5.05 \pm 0.03;\ \text{and}\ a_{H4,5,9,10} = 2.15 \pm 0.01.$$

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¹) The ESR.-spectra of the radical ions $I\cdot^{\ominus}$ and $I(2CH_3)\cdot^{\oplus}$ have also been taken at the *Institut für Organische Chemie der Universität Würzburg* [7]. Although the authors [7b] could not completely analyse the hyperfine structure of $I(2CH_3)\cdot^{\oplus}$, they independently arrived at some of the conclusions drawn by us in the discussion.

²) 1 Gauss = 10^{-4} Tesla.

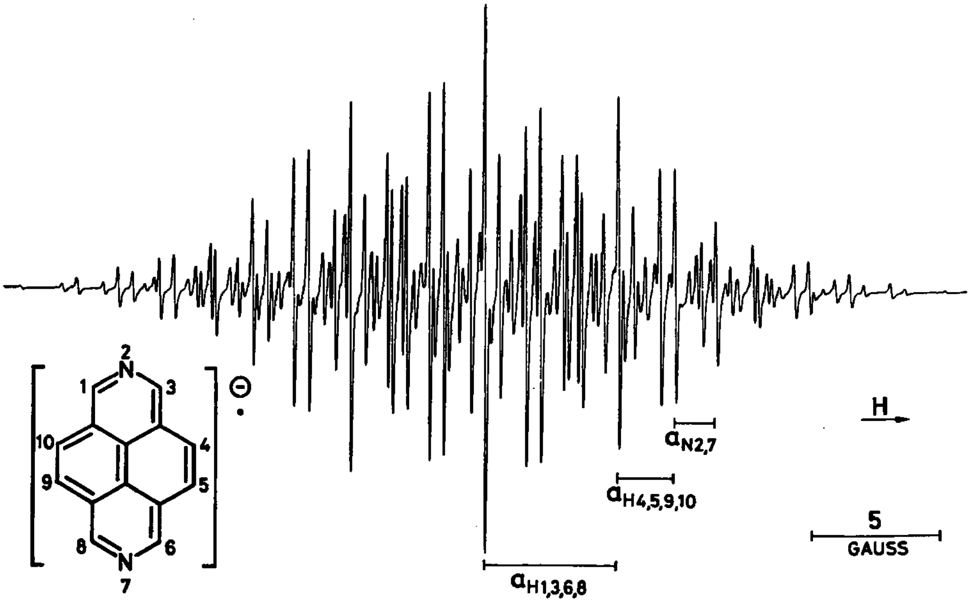

Fig. 1. *ESR.-spectrum of the radical anion* $I^{\cdot\ominus}$. Solvent: DME; counter-ion: $K^{\oplus}$; temp.: – 40°.

Assignment of the a_{H_μ} values to two sets of four equivalent protons in the positions $\mu = 1,3,6,8$ and $4,5,9,10$ is made by analogy with the corresponding ESR.-data for the radical anion of pyrene (III) [10]. Almost the same coupling constants as those given above are obtained from the ESR.-spectrum of $I^{\cdot\ominus}$ generated electrolytically in DMF [counter-ion: $(C_2H_5)_4N^{\oplus}$)].

Radical Cations $I(2H)^{\cdot\oplus}$ *and* $I(2CH_3)^{\cdot\oplus}$. Fig. 2 and 3 display the ESR.-spectra of $I(2H)^{\cdot\oplus}$ and $I(2CH_3)^{\cdot\oplus}$ formed upon reduction with zinc in methanol. The computer-simulated derivative curves, also reproduced in Fig. 2 and 3 below the respective spectra, have been plotted with the use of the following coupling constants (in Gauss2)):

$I(2H)^{\cdot\oplus}$: $a_{N2,7} = 4.04 \pm 0.03$; $a_{H2,7}$ (two NH protons) $= 4.52 \pm 0.03$;
$a_{H1,3,6,8} = 1.93 \pm 0.01$ and $a_{H4,5,9,10} = 0.41 \pm 0.01$.
$I(2CH_3)^{\cdot\oplus}$: $a_{N2,7} = 4.70 \pm 0.03$; $a_{H2,7}$ (six NCH_3 protons) $= 4.39 \pm 0.03$;
$a_{H1,3,6,8} = 1.83 \pm 0.01$ and $a_{H4,5,9,10} = 0.40 \pm 0.01$.

For both radical cations, the assignment of the a_{H_μ} values to the two sets of four equivalent protons in the positions $\mu = 1,3,6,8$ and $4,5,9,10$ is based on MO models presented in the discussion. It is noteworthy that the ratios $a_{N2,7}/a_{H2,7}$, which are $4.04/4.52 = 0.89$ for $I(2H)^{\cdot\oplus}$ and $4.70/4.39 = 1.07$ for $I(2CH_3)^{\cdot\oplus}$, compare favourably with the ratios of analogous coupling constants reported in the literature. Such ratios amount to 0.91 ± 0.04 for aromatic radical cations containing NH groups [2] [4] or NH_2 substituents [11], and to 1.06 ± 0.04 for those having correspondingly NCH_3 groups [12] or $N(CH_3)_2$ substituents [13].

Only slight deviations from the coupling constants a_{N_μ} and a_{H_μ} listed above are found in the ESR.-spectra taken of the two radical cations under different conditions, i.e., for $I(2H)^{\cdot\oplus}$ and $I(2CH_3)^{\cdot\oplus}$ in 80 percent acetic acid, as well as for $I(2CH_3)^{\cdot\oplus}$ generated electrolytically in DMF (see Experimental Part). However, a distinct

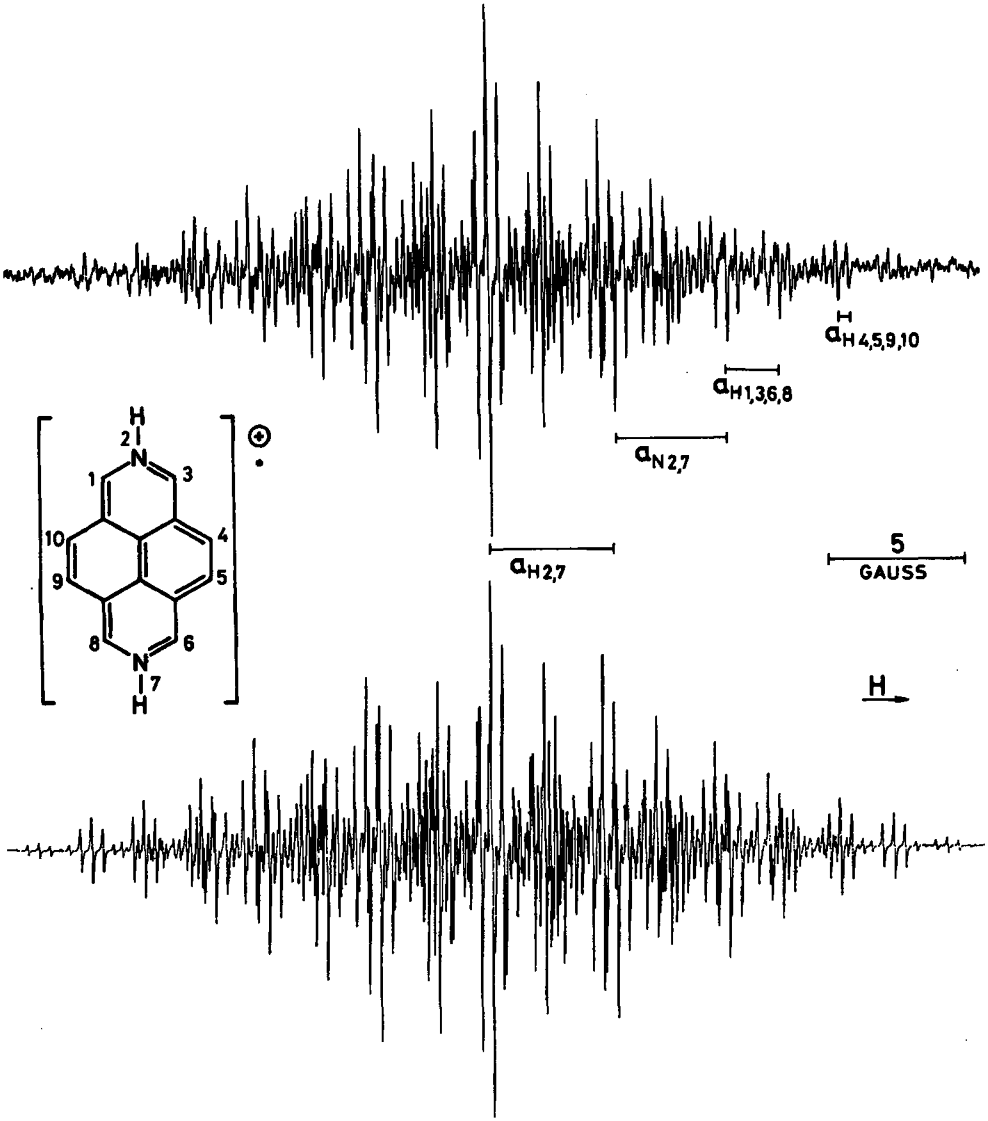

Fig. 2. *ESR.-spectra of the radical cation I(2H)* $\cdot^{\oplus}$. Top: Experimental spectrum. Solvent: methanol; temp.: + 25°. Bottom: Computer-simulated spectrum. Coupling constants given in the text; line-width: 0.05 Gauss; line-shape: Lorentzian.

line-width effect is observed in the spectrum of I(2H)$\cdot^{\oplus}$ at room temperature when methanol is replaced as solvent by 80 percent acetic acid.

This effect consists in a specific line-broadening on the wings relative to the centre of the spectrum, and, in addition, on the high- relative to the low-field side. Such a broadening is known to arise from an appreciable ^{14}N hyperfine anisotropy combined with *g* anisotropy [14]. Accordingly, the line-widths (ΔH in Gauss) under consideration could be computer-simulated with the aid of the equation

$$\Delta H = A + BM_I + CM_I^2 \tag{1}$$

where A = 0.09 ± 0.01; B = − 0.017 ± 0.003 and C = 0.032 ± 0.003. The magnetic quantum numbers $M_I = 0, \pm 1$ and ± 2, which refer to the pair of equivalent ^{14}N nuclei in I(2H) $\cdot^{\oplus}$, must be positive and negative on the low- and high-field side of the spectrum, respectively. This assignment accounts for the observed differences in the line-widths on the two sides. It is also consistent with a positive sign of the π-spin populations at the nitrogen centres and therewith of the coupling constant $a_{N2,7}$ [14] [15].

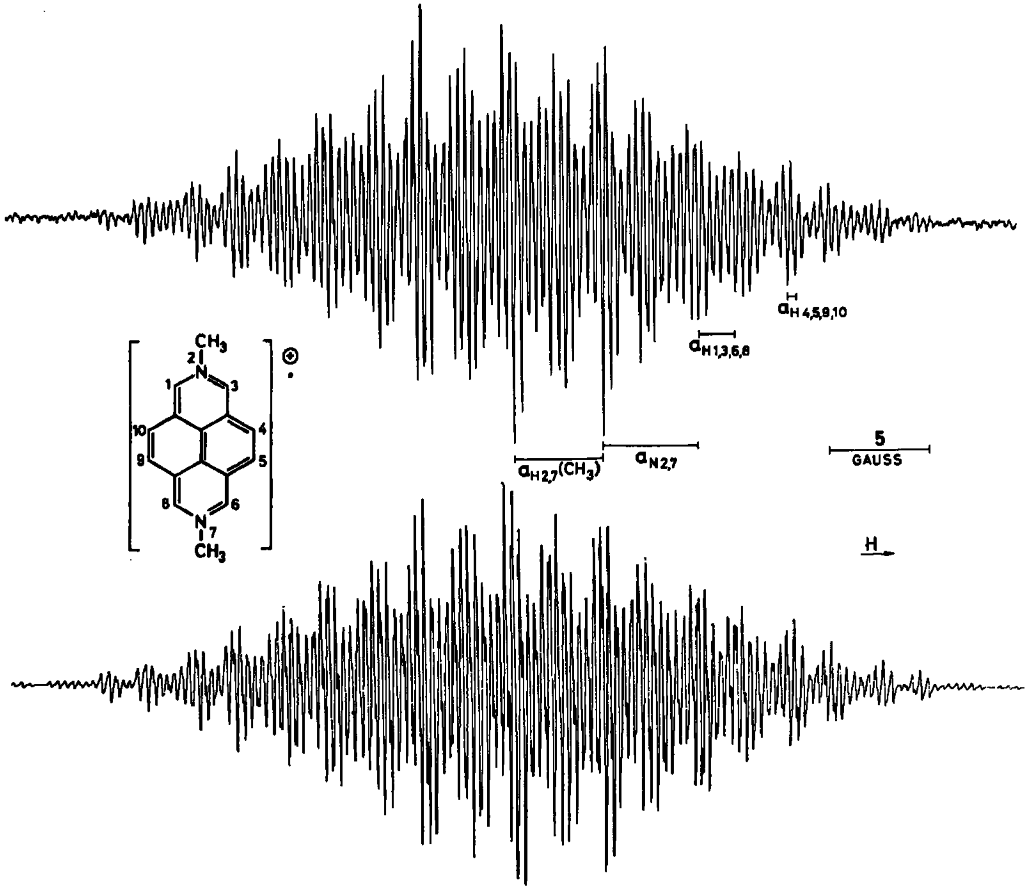

Fig. 3. *ESR.-spectra of the radical cation $I(2CH_3)^{\cdot\oplus}$.* Top: Experimental spectrum. Solvent: methanol; temp.: + 5°. Bottom: Computer-simulated spectrum. Coupling constants given in the text; line-width: 0.08 Gauss; line-shape: Lorentzian.

Discussion. – Fig. 4 summarizes the ^{14}N and proton coupling constants (a_{N_μ} and a_{H_μ}) for two series of radical ions which possess the π-topologies of pyrene (III) and biphenyl (IV), respectively. The pyrene series consists of $III^{\cdot\ominus}$ [10], followed by its iso-π-electronic diaza-derivatives $I^{\cdot\ominus}$, $I(2H)^{\cdot\oplus}$ and $I(2CH_3)^{\cdot\oplus}$ [this work], while the biphenyl series analogously embraces $IV^{\cdot\ominus}$ [16], along with its diaza-derivatives $II^{\cdot\ominus}$ [17], $II(2H)^{\cdot\oplus}$ [4] and $II(2CH_3)^{\cdot\oplus}$ [12]. The members of each series differ in the electronegativity of the azasubstituted centres which are 2 and 7 in III, or 4 and 4′ in IV, the two latter corresponding to 1 and 1′ in II (cf. the pertinent formulas). The electronegativity of these two centres increases in the sequences $III^{\cdot\ominus} < I^{\cdot\ominus} < I(2H)^{\cdot\oplus} \approx I(2CH_3)^{\cdot\oplus}$ and $IV^{\cdot\ominus} < II^{\cdot\ominus} < II(2H)^{\cdot\oplus} \approx II(2CH_3)^{\cdot\oplus}$.

Comparison of the a_{N_μ} and a_{H_μ} values in the biphenyl series supports the statement (made in the introduction) that the π-spin populations are similar throughout the whole sequence of the four radical ions. In contrast, consideration of the cor-

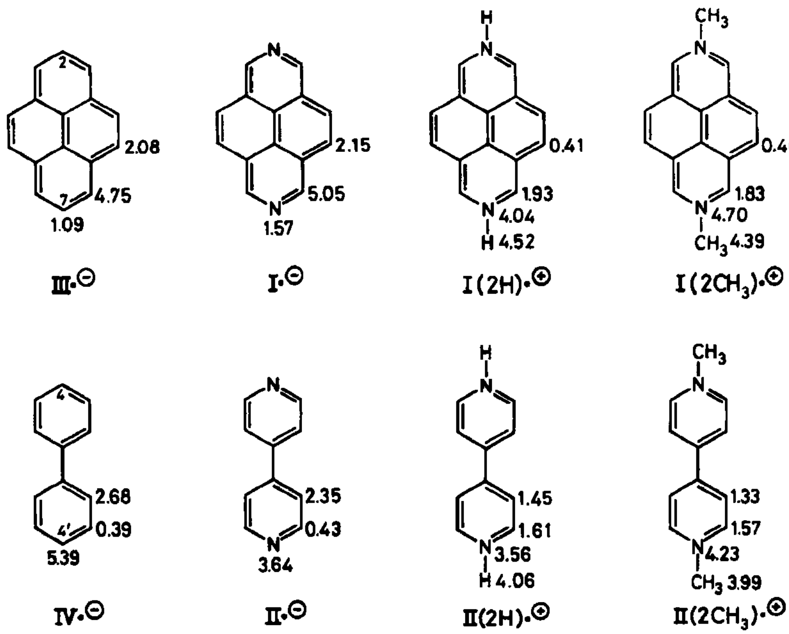

Fig. 4. *^{14}N and proton coupling constants for radical ions in the pyrene* [III · ⊖, I · ⊖, I(2H) · ⊕, I(2CH_3) · ⊕] *and biphenyl series* [IV · ⊖, II · ⊖, I(2H) · ⊕, I(2CH_3) · ⊕]. For II(2CH_3) · ⊕ our assignment of the a_{H_μ} values of 1.57 and 1.33 Gauss is opposite to that suggested originally [12].

responding data in the pyrene series indicates that a striking change occurs in the π-spin distribution on passing from the radical anions III·⊖ and I·⊖ to the radical cations I(2H)·⊕ and I(2CH_3)·⊕. As a matter of fact, the values $a_{N2,7}$ for I(2H)·⊕ and I(2CH_3)·⊕, while vastly different from that for I·⊖, strongly resemble the corresponding ^{14}N coupling constants for II(2H)·⊕ and II(2CH_3)·⊕. These experimental findings are readily rationalized by means of a simple HMO model.

The two lowest antibonding HMO's of pyrene (III) are depicted in Fig. 5, together with the corresponding HMO's of biphenyl (IV). They have been classified as symmetric (ψ_S) or antisymmetric (ψ_A) with respect to the mirror planes (m) which are perpendicular to the molecular plane and pass through the centres 2 and 7 (III) or 4 and 4' (IV). Fig. 5 also displays the energy sequence of ψ_S and ψ_A in two π-systems: ψ_S above ψ_A in III ($E_S = \alpha - 0.879\beta$; $E_A = \alpha - 0.445\beta$) and ψ_S below ψ_A in IV ($E_S = \alpha - 0.705\beta$; $E_A = \alpha - \beta$)[3]).

An increase in the electronegativity of the centres 2 and 7 (III) or 4 and 4' (IV) strongly stabilises the HMO's ψ_S by an amount of energy which – to the first order approximation – is given as

$$dE_S = (c_{S2}^2 + c_{S7}^2)d\alpha = 2c_{S2}^2 d\alpha \qquad (2)$$

or

$$dE_S = (c_{S4}^2 + c_{S4'}^2)d\alpha = 2c_{S4}^2 d\alpha \qquad (3)$$

respectively, where $c_{S2} = c_{S7} = 0.424$ (III) or $c_{S4} = c_{S4'} = 0.398$ (IV) denote the pertinent LCAO coefficients, and dα stands for the change in the *Coulomb* integral of

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[3]) The HMO model of IV exhibits two accidentally degenerate orbitals with the energy $E_A = \alpha - \beta$. Both of them, ψ_A (which is depicted in Fig. 5) and $\psi_{A'}$ are antisymmetric with respect to the mirror plane m.

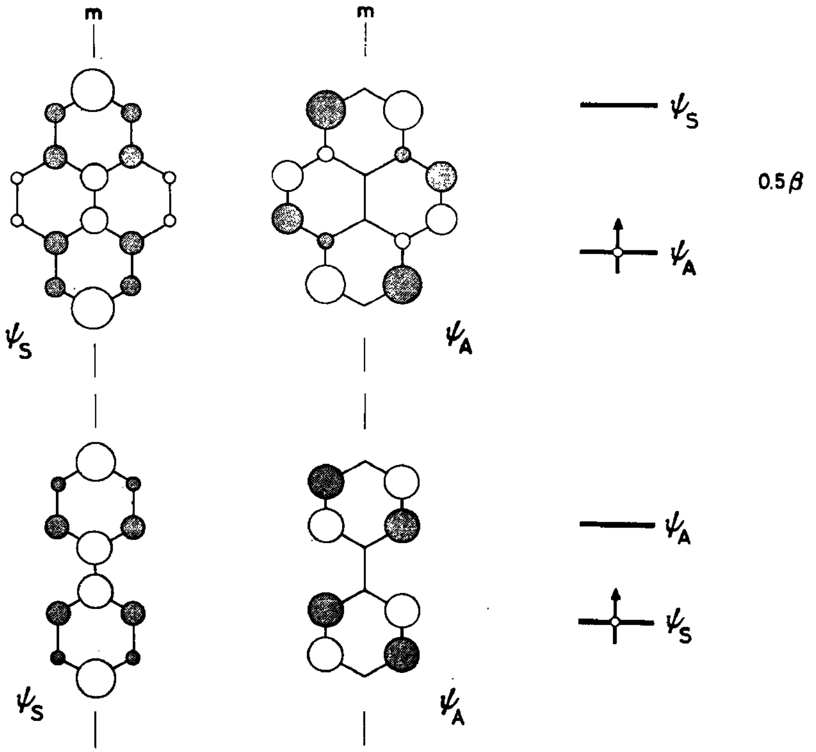

Fig. 5. *The two lowest antibonding HMO's* (ψ_S and ψ_A) *of pyrene* (III) *and biphenyl* (IV). The radii of the circles are proportional to the absolute values of the LCAO coefficients. Blank and dotted areas symbolise different signs. The levels on the right indicate the energy sequence of ψ_S and ψ_A in III and IV. The arrows mark the orbital occupancy in the corresponding radical anions III $\cdot^{\ominus}$ and IV $\cdot^{\ominus}$.

the two centres under consideration. On the other hand, no substantial lowering in energy arises from such an increase for the antisymmetric HMO's ψ_A, since $c_{A2} = c_{A7}$ (III) and $c_{A4'} = c_{A4}$ (IV) vanish, and hence $dE_A = 0$, to the first approximation.4)

As ψ_S lies below ψ_A in IV, the difference $E_A - E_S$ ($= -0.295\beta$) is enlarged when the centres 4 and 4' are made more electronegative; however, the energy sequence of ψ_S and ψ_A is preserved. On the contrary, since ψ_S is placed above ψ_A in III, the gap $E_S - E_A$ ($= -0.434\beta$) is reduced by an increase in electronegativity of the corresponding centres 2 and 7; the energy sequence of ψ_S and ψ_A can thus be reversed, provided that such an increase is sufficiently large. The HMO models allow the following predictions to be made:

1. In the biphenyl series, the singly occupied orbital of all four radical ions, IV$\cdot^{\ominus}$, II$\cdot^{\ominus}$, II(2H)$\cdot^{\oplus}$ and II(2CH$_3$)$\cdot^{\oplus}$ should resemble the symmetric HMO ψ_S of IV.

2. In the pyrene series, a change in the shape of the singly occupied orbital must be envisaged while proceeding along the sequence III$\cdot^{\ominus}$ < I$\cdot^{\ominus}$ < I(2H)$\cdot^{\oplus}$ ≈ I(2CH$_3$)$\cdot^{\oplus}$ of increasing electronegativity. Such a change would imply a replacement of an

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4) In the case of IV, the same holds for the antisymmetric HMO $\psi_{A'}$ which in the model of IV is accidentally degenerate with ψ_A (see footnote 3); thus for $\psi_{A'}$, too: $c_{A'4} = c_{A'4'} = 0$ and $dE_{A'} = 0$.

orbital with the nodal properties of the antisymmetric HMO ψ_A of III by the one resembling the symmetric HMO ψ_S of this π-system.

Both predictions have been amply confirmed by experiment, as can be readily verified by inspection of Fig. 4 and 5. It is obvious that the hyperfine data for all four radical ions in the biphenyl series are consistent with the single occupancy of a ψ_S-like orbital[5]).

The change in the symmetry of the singly occupied orbital predicted for the pyrene series is clearly borne out by the striking difference in the coupling constants for III$^{\cdot\ominus}$ and I$^{\cdot\ominus}$, on one hand, and those for I(2H)$^{\cdot\oplus}$ and I(2CH$_3$)$^{\cdot\oplus}$ on the other. The ESR.-data establish that the relevant orbitals in the two radical anions and the two radical cations are of the ψ_A- and ψ_S-type, respectively. Moreover, the similarity in the coupling constants, which has been noted for the corresponding radical cations in the two series, nicely reflects the almost identical nodal properties of the symmetric HMO's ψ_S of pyrene and biphenyl (Fig. 5).

The reversal in the sequence of ψ_S and ψ_A in the pyrene series can be assessed "more quantitatively" if the energies $E = \alpha + x\beta$ of the two HMO's are plotted vs. the change $d\alpha = h\beta$ in the Coulomb integral of the centres 2 and 7. As evident from Fig. 6, ψ_S becomes equal in energy to ψ_A at $h = 0.434/[2(0.424)^2] \approx 1.21$ when the first order approximation formula (2) is used, or at $h \approx 1.45$ when the HMO matrices are diagonalized for every value of h. This result is very reasonable, since either value for the crossing point of ψ_S and ψ_A lies between the h ranges characteristic of an unprotonated ($0.5 \leqslant h_{\dot{N}} \leqslant 1.0$) and a protonated nitrogen center ($1.5 \leqslant h_{\overset{+}{N}} \leqslant 2.0$) [18].

The assignment of the proton coupling constants $a_{H1,3,6,8}$ and $a_{H4,5,9,10}$ for the radical cations I(2H)$^{\cdot\oplus}$ and I(2CH$_3$)$^{\cdot\oplus}$ has been based on the π-spin distribution resulting from the single occupancy of the HMO ψ_S. Since – irrespective of the choice of the parameter h – the π-spin populations are predicted to be higher at the centres 1,3,6,8 than at 4,5,9,10, the larger a_{H_μ} values have been assigned to the protons in the former, and the smaller ones to those in the latter positions.

A final comment concerns the line-width effect observed for I(2H)$^{\cdot\oplus}$ in 80 percent acetic at + 25°. As such an effect is promoted by a substantial ^{14}N hyperfine anisotropy and a long rotational correlation time, it has been encountered, in general, with large ^{14}N coupling constants ($a_{N_\mu} \approx 10$ Gauss) and/or bulky radicals in rather viscous solvents. In the case of I(2H)$^{\cdot\oplus}$, the $a_{N2,7}$ value (4.04 Gauss) is not particularly large; neither has the radical cation a considerable size. Although the viscosity of 80 percent acetic acid at + 25° (1.5 ± 0.2 cP[6])) [19a] is estimated to be *ca.* 3 times as high as that of the alternative solvent methanol (0.55 cP) [19b], it is by no means excessive. Typically, the dimethyl-derivative I(2CH$_3$)$^{\cdot\oplus}$, which possesses both a larger coupling constant $a_{N2,7}$ (4.70 Gauss) and a greater size than I(2H)$^{\cdot\oplus}$, does not exhibit a comparably marked line-width effect when its ESR.-spectrum is taken under the same conditions. It may be thus assumed that specific solute-solvent interactions play an important role for I(2H)$^{\cdot\oplus}$ in 80 percent acetic acid. Such interactions as, e.g., momentary $>\!N{-}H{-}{-}{-}O{=}C\!<$

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[5]) It should be stated at this point that the behaviour of the HMO's ψ_S and ψ_A in the biphenyl series is characteristic also of other π-systems representing the azaaromatic compounds previously studied which yield both radical anions and dihydro radical cations (pyrazine, s-tetrazine, quinoxaline and phenazine) [1]–[5]. Since the lowest antibonding HMO's in these π-systems exhibit relatively large coefficients at the azasubstituted π-centres, they are more strongly stabilized by an increase in the electronegativity of such centres than the next higher lying HMO's of different symmetry.

[6]) 1 cP (Centipoise) $= 10^{-3}$ kgm^{-1} sec^{-1}.

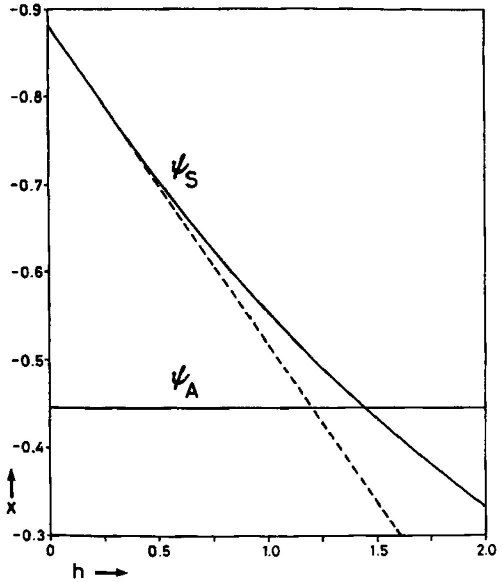

Fig. 6. *HMO energies* [$x = (E - \alpha)/\beta$] *of pyrene* (III) *vs. the change in the Coulomb integral* ($h = d\alpha/\beta$) *of the centres 2 and 7.* The dashed line results from the use of equation (2).

hydrogen bonds, can considerably increase the rotational correlation time and thus contribute to the line-width in the ESR.-spectra.

We thank Prof. *W. Jenny*, Ciba-Geigy SA, Basel, for a sample of 2,7-diazapyrene (I) and Mr. *G. Plattner* of our Institute for a computer program which simulates ESR.-spectra with varying line-width. We are also indebted to Prof. *S. Hünig*, Universität Würzburg, for communicating the unpublished results [7] of ESR.-studies carried out in his Department. Support by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Project Nr. 2.163.74) is acknowledged, as well as the financial assistance of Ciba-Geigy SA, Sandoz SA and Hoffmann-La Roche SA.

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262. The Radical Ions of Benzo[b]biphenylene, a Test for HMO Models of Biphenylene and its Derivatives

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Summary. ESR.-spectra are reported for the radical anion and the radical cation of benzo[*b*]-biphenylene (III). Comparison of the proton coupling constants (a_{H_μ}) for III · $^{\ominus}$ and III · $^{\oplus}$ with π-spin populations (ϱ_μ), calculated by the *McLachlan* procedure, permits a lower limit of 0.77 to be set for the parameter $k = \beta'/\beta$ where β' represents a reduced value of the HMO integral for the two essentially single bonds linking the benzene with the naphthalene π-system. The differences in the a_{H_μ} values for III · $^{\ominus}$ and III · $^{\oplus}$ are substantially larger than those generally found for the two corresponding radical ions of alternant, purely benzenoid hydrocarbons, but they closely parallel the analogous differences observed for the radical anion and the radical cation of biphenylene.

Biphenylene (I) and binaphthylene (II) are usually regarded as weakly coupled benzenoid π-systems rather than as derivatives of cyclobutadiene. Such an approach is supported by both theory [1] and X-ray structure analysis [2] which indicate that the two bonds linking the benzene or naphthalene π-systems are essentially single. The latter statement also applies to the radical ions of I and II, although the double bond character of the two linkages (4a–4b and 8a–8b in I or 5a–5b and 11a–11b in II) is expected to be enhanced in these ions relative to the respective neutral compounds. It may thus be anticipated that – in order to achieve agreement with experiment – the HMO treatment of the radical ions of I and II would require a reduced bond integral for the linkages in question. Such a reduced integral will henceforth be denoted $\beta' = k\beta$ where β is the standard value and the parameter $k \leqslant 1$. In principle, it should be possible to estimate k by comparing the known proton coupling constants (a_{H_μ}) for the radical ions I·$^{\ominus}$, I·$^{\oplus}$ and II·$^{\ominus}$ [3–5] (see also Appendix) with the theoretical π-spin populations (ϱ_μ). Such a comparison is, however, rather inconclusive with respect to k, because the ϱ_μ values calculated for the radical ions of I and II, either in the HMO or *McLachlan* [6] approximation, are not very sensitive to variation of k in the range between 1.0 and 0.5.

It will be shown in the present paper that an analogous comparison is more informative in the case of the radical ions of benzo[*b*]binaphthylene (III) where the

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