On the Homoconjugation of Two Acceptor Groups

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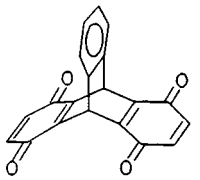
Received March 4, 1998

Keywords: Homoconjugation / Cyclovoltammetry / ESR spectroscopy / Diketones / Heterocycles

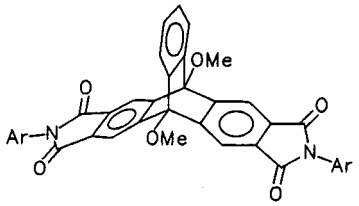
Cyclovoltammetric investigations have been carried out on 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetrone (**4**), bicyclo-[3.2.2]nonane-6,7,8,9-tetrone (**5**), and several of their congeners, such as 6,13-dihydro-6,6,13,13-tetramethylquinoxalino[2.3-*b*]phenazine (**13**), 5,10-dihydro-5,5,10,10-tetramethylpyrazino[2,3-*g*]quinoxaline (**17**), and 6,13-dihydro-6,13-propanoquinoxalino[2,3-*b*]phenazine (**20**). For **5** and **20** a large difference ($\Delta E°$ ≥400 mV) between the first and second reduction potentials was found. The ESR results of the radical anion **20**$^{\bullet-}$ are in support of a strong homoconjugation. ESR studies of **4**$^{\bullet-}$, **13**$^{\bullet-}$, and **17**$^{\bullet-}$ also reveal a symmetrical displacement of the unpaired electron over both acceptor groups on the ESR time scale which, however, based on the small potential difference $\Delta E° \leq 200$ mV can be most likely described to a fast electron exchange.

Cyclic voltammetry (CV) is a proper means to investigate the electron affinity of molecules in solution.With some assumptions the measured reduction potential can be correlated with the energy of the lowest unoccupied molecular orbital (LUMO). The reduction potential is also related to the thermodynamic stability of the corresponding radical anion[1][2][3]. Of special interest are CV investigations of molecules in which two identical acceptor groups are separated by sp^3 centers. In such cases a large difference between the first two reduction potentials is indicative of the delocalization of the unpaired electron[4]. In cases where the unpaired electron is localized in only one acceptor moiety it is argued that it should influence the second reduction potential less than in cases where the electron is delocalized over both acceptor groups[5]. For example, in the cases of **1** and **2,** where the radical anion is found to be localized in one fragment under the experimental conditions used, the energy for introducing a second electron is about half than that in **3**, where the unpaired electron is delocalized over the whole molecule[4][5]. The method of choice to investigate the delocalization of an unpaired electron is electron spin resonance (ESR) spectroscopy[6][7][8]. It shows, via the hyperfine structure in the spectrum, which nuclei are interacting with the unpaired electron and thus allows the spatial distribution of this electron to be determined.



1

ΔE^0 (mV) = 230 mV



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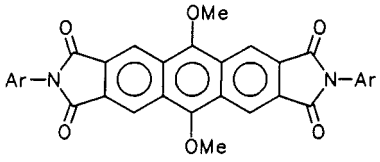
ΔE^0 (mV) = 160 mV

Ar = 4-*tert*-butylphenyl



3

ΔE^0 (mV) = 440 mV

Ar = 4-*tert*-butylphenyl

Recently we reported the synthesis and properties of some bisdiketones in connection with our studies on bishomosquaric acid derivatives[9]. Derivatives, **7** and **8**, could each be prepared by irradiation of 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetrone (**4**) and bicyclo[3.2.2]nonane-6,7,8,9-tetrone (**5**), respectively, in the presence of tetramethylethylene (**6**) (Scheme 1)[9]. Photoelectron-spectroscopic investigations in the gas phase revealed strong interactions between the two diketone moieties in **4** and **5**, while no interaction between the donor and acceptor units in **7** and **8** could be detected[9].The strong interactions of the two acceptor moieties in **4** and **5** prompted us to prepare several derivatives of both compounds and to investigate their properties as electron acceptors by cyclic voltammetry and by studying the ESR spectra of the radical anions, formed by one-electron reductions.

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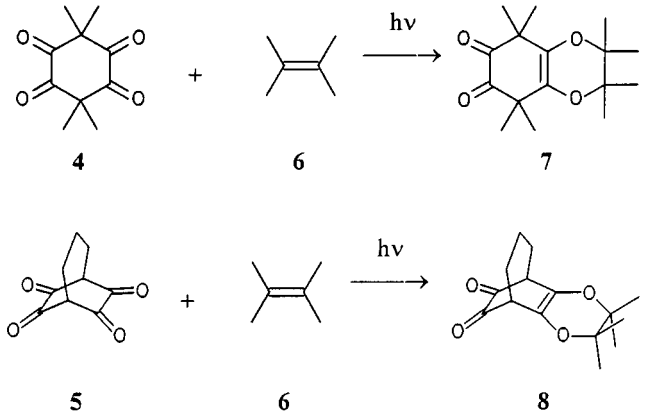
Scheme 1



1. Cyclovoltammetric Investigations

1.1 Investigations of Systems with Two Acceptor Groups

The model compounds which were studied are **4** and some derivatives whose syntheses are described in Section 3 of this paper. For comparison we also included 3,3,6,6-tetramethylcyclohexane-1,2-dione (**9**) and its diiminoderivatives **10**−**12** in our investigations. In Table 1 we compare the first two reduction potentials of **4** with those measured in **9**−**12**. In the case of **9** and **11** only one reduction potential was seen. All reductions were carried out in DMF, using ferrocene for calibration. We observed two reversible reduction potentials for **4** (see Figure 1). The first one is less negative by 415 mV than that of **9** which indicates that the reduction of one diketone unit in **4** is influenced considerably by the presence of the second one, in other words: the C_2O_2 unit shows a strong inductive effect on its close neighbors. The influence of the quinoxaline- and pyrazine-units in **10** and **11**, respectively, upon the diketone is similar.

The second reduction potential of **4** is separated only by 195 mV from the first one. Following the criteria proposed by Miller et al.[4] this result suggests that the unpaired electron in the radical anion of **4** might be localized in one diketone unit. In line with this argument is the observation that the second reduction step still takes less energy (+220 mV) than the first reduction of **9**. A second reduction is also encountered in **10** around 1600 mV. We ascribe this to the reduction of the quinoxaline fragment (see below).

In the central part of Table 1 the data obtained for the reduction of the quinoxaline derivatives **12**−**15** are compiled. The comparison between the first reduction potential of **12** with that of **13** shows that a second acceptor unit decreases the first reduction potential by 195 mV. Similarly, the first reduction potentials of **14** and **15** are lower by 160 and 175 mV, respectively, than that of **12**. The difference between the first and second reduction steps of **13** (see Figure 1) is found to be 185 mV, which is in accordance with the results on **4**. Therefore the corresponding radical anion might also be localized in one part of the molecule[4].

During the reduction of **13** in DMF we observed a dependence of the second reduction peak on the concentration of **13**. At low concentrations we found two peaks

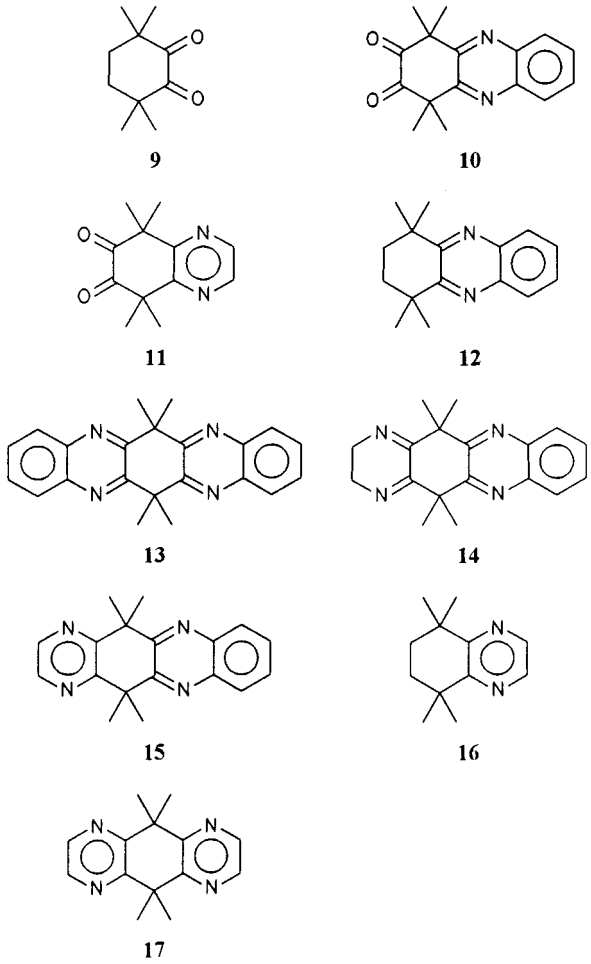


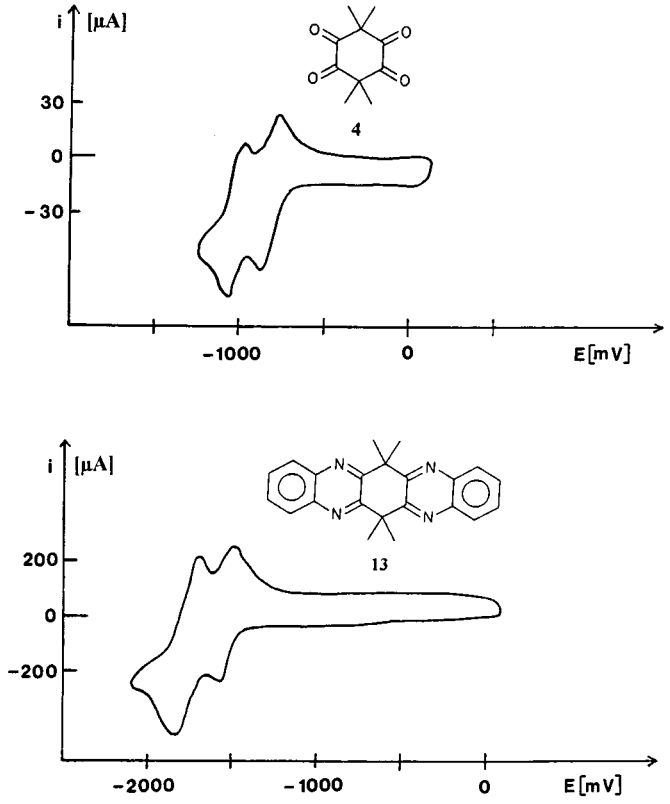
Table 1. Reduction potentials E^0_{red} of **4**, **5**, and **9**−**20** in DMF. The differences between these reduction potentials and those of **9**, **12**, **16**, **18**, and **19** as appropriate ($E^0_{red,1}$), and the differences between the first and second reduction potentials (ΔE^0) of each compound are given. All values in mV

Compound	$E^0_{red,1}$	$\Delta E^0_{red,1}$	$E^0_{red,2}$	ΔE^0
9	−1320	−	−	−
4	−905	+415	−1100	+195
10	−1065	+255	−1600	+280
11	−1070	+250	−	−
12	−1780	−	−	−
13	−1585	+195	−1770	+185
14	−1620	+160	−1790	−
15	−1605	+175	−2200	−
16	−2270	−	−	−
17	−2015	+255	−2210	+195
18	−1280	−	−	−
5	−730	+550	(−1750)[a]	(+980)[b]
19	−1820	−	−	−
20	−1540	+280	−1940	+400

[a] Irreversible, maximum of reduction current. − [b] Difference of the maxima of the reduction current.

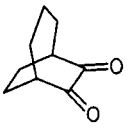
$E_{red,2}$ = −1770 mV and $E_{red,2'}$ = 1905 mV. At larger concentrations the peak at −1770 mV decreased and finally only the one at −1095 mV remained. To rationalize this behavior we assume an aggregation of $\mathbf{13}^{\bullet-}$ to $(\mathbf{13})_2^{2-}$ at higher concentrations.

Figure 1. CV of **4** (top) and **13** (bottom) in DMF; v = 100 mV/sec



The reduction of **17** in DMF yields two potentials which are 195 mV apart. The generation of the radical anion **17**$^{\bullet-}$ occurs at lower energy (255 mV) than that of **16** (Table 1).

The reduction of **18** was reversible and showed one peak at −1280 mV. The value is similar to that measured for **9**. The reduction of **5** was also reversible and showed a peak at $E_{red,1}$ = 730 mV (see Table 1). The reoxidation current was strongly dependent on the scan speed. At large scan speeds (≥ 2000 mV/sec) both peak currents $i_{m,red}$ and $i_{m,ox}$ were about the same size, which is indicative of a reversible reaction. At lower scan speeds the height of the back-oxidation current was decreased. At 50 mV/sec $i_{m,ox}$ is about one third of $i_{m,red}$. We rationalize this behavior by assuming that, after formation, the radical anion reacts further; but at high scan speeds the rate of back-oxidation is faster than the rate of the reaction.



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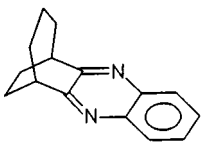

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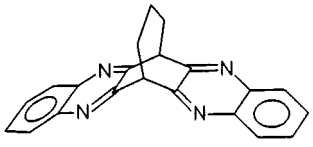
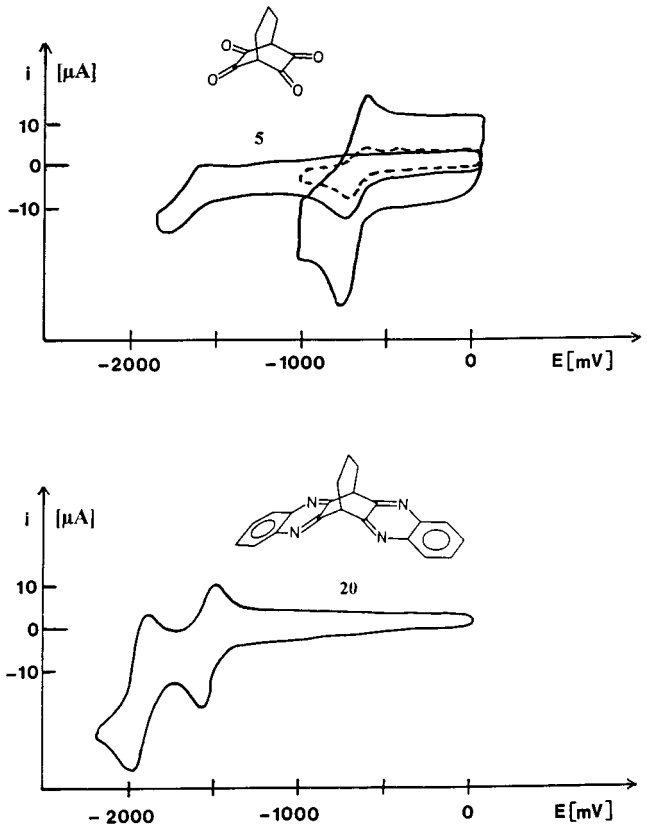


20

Figure 2. CV of **5** (top) and **20** (bottom) in DMF. In the case of **5** the CV of the one electron reduction is given for v = 2000mV/sec (full line) and v = 100 mV/sec (dotted line). A second reduction is found at ca. −1750 mV (v = 100 mV/sec)



At about −1750 mV (100 mV/sec) a further reduction was found (see Figure 2). The separation of the peaks for reduction (1750 mV) and oxidation (1610) is rather large and points to a non-reversible reaction for the second reduction step. We assume that a fast reaction follows the second reduction of **5**.

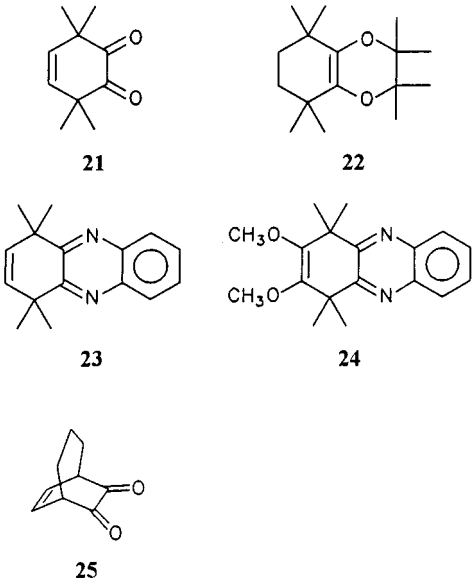
For **5** we notice a large difference ΔE^0 = 980 mV between the two reduction steps. This difference is considerably larger than that for **4** (195 mV). In addition the first reduction takes place at less negative potential compared to **4**, both when looking at the absolute values (Δ = 175 mV), and when looking at the differences with the corresponding diketones (Δ = 135 mV). These findings point to a complete delocalization of the unpaired electron in the radical anion of **5**.

The cyclovoltammogram of **20** showed two reduction peaks that are reversible at low concentrations (Figure 2). As anticipated from the comparison between **13** and **12**, we found for **20** that the first reduction took less energy (280 mV) than that for **19**. At higher concentration of **20** we observed an increase of the intensity of the second redox-wave at −1940 mV. Similar behavior was also observed in the case of **13**. We assume for the dianion of **20** that aggregates were formed. It is interesting to note that the difference ΔE^0 found for **20** amounts to 400 mV. This difference is indicative of a delocalized radical anion[4].

A comparison between the results obtained for **4** and **13** with those of **5** and **20** might suggest that a rigid bicyclic structure favors a delocalization of the radical anion. However, this argument can be invalidated by looking at the ΔE values of **1**−**3**. Here the bicyclic structure of **1** and **2** does not favor a delocalization of the radical anion[4].

1.2. Investigations of Donor-Acceptor Systems

To explore the possibility of homoconjugation in the radical anion of compounds with donor and acceptor groups, we investigated the redox potentials of **7** and **8** (see Figure 3). For comparison we also measured the redox potentials of related species such as **9** and **18** as well as **21**, **22**, and **25** (see Table 2). To judge the interactions in **7**, we compared its redox potentials with those of **9**, **21**, and **22** (Table 2), which were recorded in methylenchloride as solvent. The reduction potentials of **7** and **21** were by about 100 mV lower than that of **9**. We ascribe this small variance to a difference in the dihedral angle between the saturated (**9**) and unsaturated (**7**, **21**) systems, since the energy of the lowest π* molecular orbital of a C_2O_2 moiety depends strongly on the dihedral angle between the CO groups.



The reduction potentials (recorded in DMF) of **12** (−1780 mV), **23** (−1735 mV), and **24** (−1700 mV) confirm the data obtained for **7**, **9**, and **21**, in so far as they also show very small differences between the saturated (**12**) and the unsaturated (**23**, **24**) derivatives. Our argument that the small differences in the reduction potential between **7** and **21** on one hand, and **9** on the other is due to a smaller dihedral angle between the CO-groups in the former than in the latter is supported by comparison of the reduction potentials of **8**, **18**, and **25**. In the bicyclic systems we expect very similar dihedral angles, due to the high rigidity of this system.

The oxidation of the donor fragment takes 425 mV more energy in **7** than in **22**. This is in line with our previous

Figure 3. CV of **7**, **8** (full line) and **22** (broken line) in DMF; v = 100 mV/sec

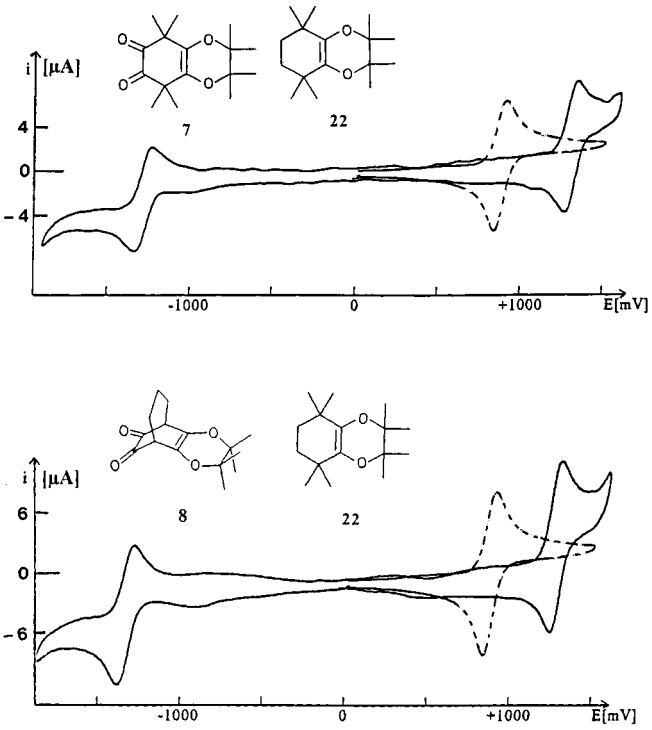


Table 2. Comparison of the redox potentials (E^0_{red}, E^0_{ox}) of **7** with the model systems **9**, **21**, and **22** as well as of **8** with **18** and **25**. The values were measured in CH_2Cl_2, all values in mV

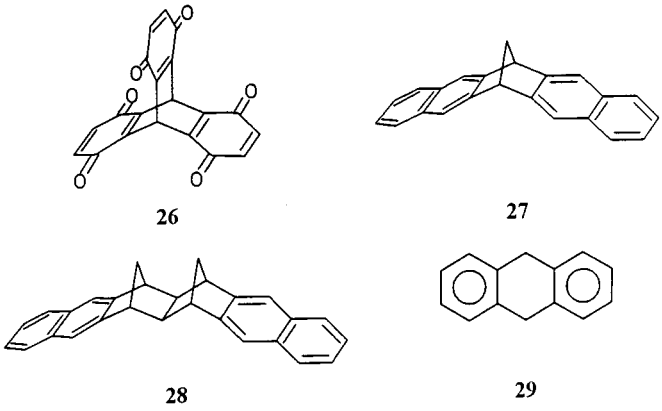
Compound	E^0_{red}	E^0_{ox}
7	−1285	+1305
9	−1400	−
21	−1300	−
22	−	+880
8	−1335	+1255
18	−1325	−
25	−1330	−

experience in the systems with two acceptor moieties: The C_2O_2 unit shows a strong (inductive) effect on its close neighbors. No sign of homo conjugation between donor and acceptor groups in **7** and **8** is observed.

2. ESR-Spectroscopic Investigations

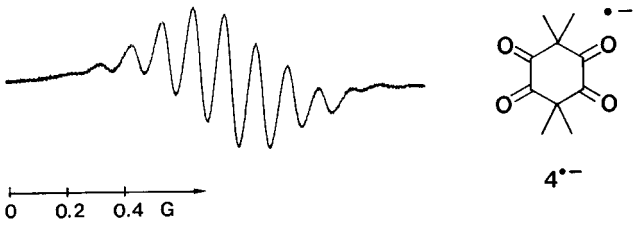
2.1 Systems with Two Acceptor Groups

Various radical anions with two identical, non-conjugated acceptor groups have been investigated by ESR spectroscopy. Representative examples are $\mathbf{1}^{\bullet-}$[10], $\mathbf{2}^{\bullet-}$[4], and $\mathbf{26}^{\bullet-}$−$\mathbf{29}^{\bullet-}$[10][11][12]. These investigations have shown that, under the experimental conditions, in $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ the unpaired electron is localized in one acceptor unit, since at low temperatures only hyperfine coupling to the nuclei of one fragment is observed. However, in the radical anions of **26**−**29** it was not possible to discriminate between complete delocalization or fast electron transfer[10][11][12].



To explore the delocalization of the unpaired electron in the radical anions of **4**, **5**, and related compounds in more detail, we generated the corresponding radical anions by reduction of the parent compounds with potassium in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (kryptofix® 222) as complexing agent to minimize any ion-pair formation. Their ESR spectra were interpreted by means of ENDOR spectroscopy and, where possible, triple resonance techniques[13][14].

Figure 4. ESR spectrum of the radical anion $\mathbf{4}^{\bullet-}$ in DME/kryptofix® 222 at 260 K

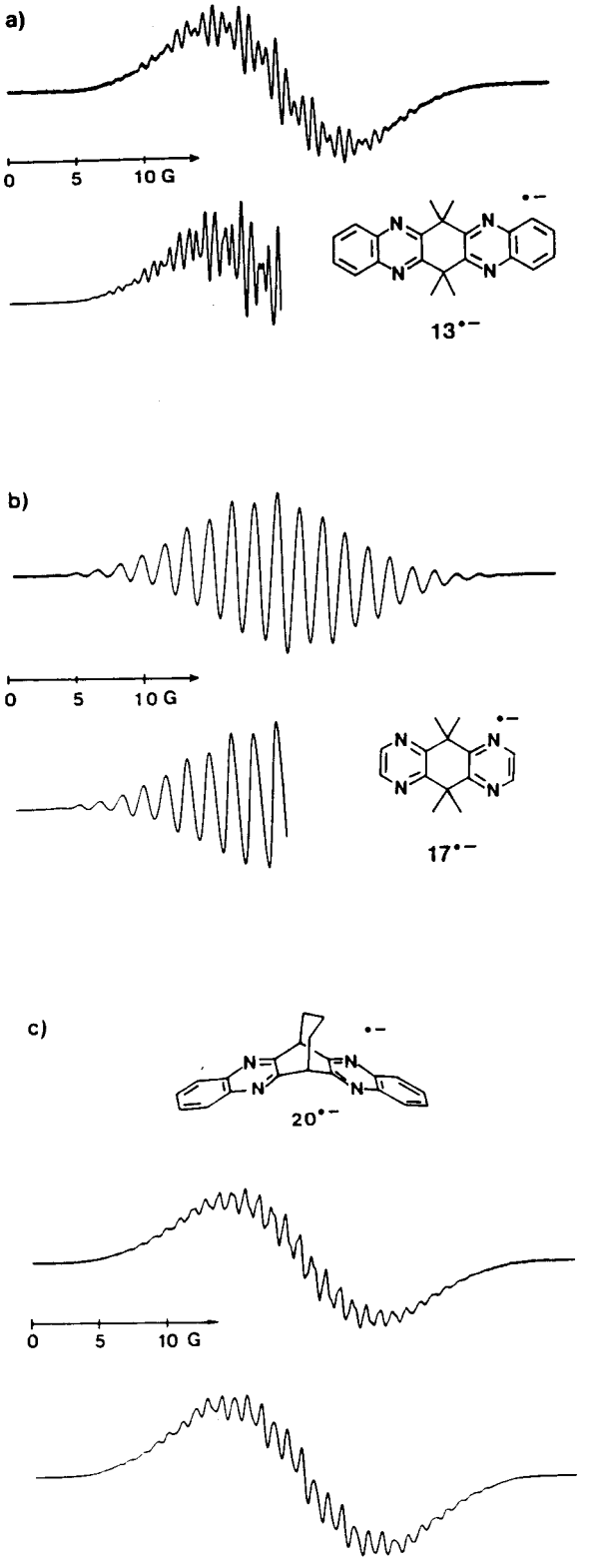


Reduction of **4** with potassium in 1,2-dimethoxyethane (DME) in the presence of kryptofix® 222 readily afforded the radical anion $\mathbf{4}^{\bullet-}$. Its ESR spectrum (Figure 4), g = 2.0054, shows the expected hyperfine coupling to 12 equivalent hydrogens with a(H) = 0.11 G. The coupling constant of the methyl hydrogens of $\mathbf{4}^{\bullet-}$ is less than half the value reported for the methyl hydrogens of the 2,2,5,5-tetramethylhexane-3,4-dione radical anion ($\mathbf{30}^{\bullet-}$), a(H) = 0.34 G in DME[15] and a(H) = 0.29 G in dimethyl sulfoxide (DMSO)[16]. Furthermore, the g value of $\mathbf{4}^{\bullet-}$ is considerably larger than those observed for $\mathbf{9}^{\bullet-}$ (g = 2.0050, see below) and for the radical anion of the parent cyclohexane-1,2-dione (g: 2.0049−2.0051) [17] but is close to g-values found for radical anions of vicinal tri- and tetraketones, e.g. 2,2,7,7-tetramethyloctane-3,4,5,6-tetrone (**31**) (g = 2.0055)[18]. We interpret the rather high g value of $\mathbf{4}^{\bullet-}$ in terms of increased spin-orbit coupling, due to the interactions between the unpaired electron and the lone-pairs at the oxygen atoms. A possible rationalization is given if we assume a delocalization of the unpaired electron over all four carbonyl groups in $\mathbf{4}^{\bullet-}$. Surprisingly, the reduction of **4** in DMSO with propiophenone and potassium *tert*-butoxide[19] yields a different radical anion with a(H) = 0.29 G (12 H, 2,2,7,7-CH_3) and g = 2.0050. These data point to an ion-paired semidione[17] in which the unpaired electron is mainly localized on one C_2O_2 unit. Our attempts to generate the radical anion $\mathbf{5}^{\bullet-}$ by reduction of the bicyclo[3.2.2-]nonane-6,7,8,9-tetrone (**5**) with potassium in DME or with propiophenone and potassium *tert*-butoxide in DMSO have failed so far, probably owing to immediate decomposition. Reduction of the diketone **9** with potassium in DME in the presence of kryptofix® 222 also afforded readily the radical anion $\mathbf{9}^{\bullet-}$. In contrast to a previous study of $\mathbf{9}^{\bullet-}$ in DMSO[20], the narrow ESR spectrum (width ca. 4 G) of $\mathbf{9}^{\bullet-}$ in DME at 270 K shows a partially resolved hyperfine structure consisting of about 21 lines. ENDOR at 210 K clearly yields three types of splittings corresponding to a(H) = 0.50, a(H) = 0.34, and a(H) = 0.20 G. The appearance of three splittings is in agreement with a half-chair conformation of $\mathbf{9}^{\bullet-}$, provided that either the splitting of one set of hydrogens is unobservable, owing to its very small size, or that two different sets of hydrogens have almost the same splitting. Attempts to simulate the observed ESR spectrum with the splittings given above led to several equally good solutions for both possibilities and were hence unsuccessful. However, the width of the ESR spectrum indicates that the splitting a(H) = 0.50 cannot be due to the six methyl hydrogens but must originate from two (or at the maximum four) hydrogens at C4 and C5. The g-value of $\mathbf{9}^{\bullet-}$ (g = 2.0050) is the same as those of related cyclic 1,2-semidiones[17].

The ESR spectrum of the similarly generated bispyrazine radical anion $\mathbf{17}^{\bullet-}$ (g = 2.0036, Figure 5b) at 250 K was well simulated with a(N) = 3.33 (4 N) and a(H) = 1.47 G (2,3,7,8-H). ^{1}H ENDOR and general triple resonance spectroscopy at 230 K yielded, besides a(H) = 1.47 G, a further small splitting of a(H) = 0.15 G, which originates from the twelve methyl hydrogens. Both hydrogen splittings have the same sign (negative). These results confirm that the unpaired electron in $\mathbf{17}^{\bullet-}$ is delocalized over the whole molecule on the ESR time scale. As expected, the major coupling constants of $\mathbf{17}^{\bullet-}$ have about half the magnitude of the corresponding splittings reported for the 2,3-dimethylpyrazine radical anion ($\mathbf{33}^{\bullet-}$; sodium, THF): a(N) = 6.66 (2 N), a(H) = 2.43 (5,6-H), a(H) = 1.76 (6 H, 2,3-CH_3), g = 2.0035[21].

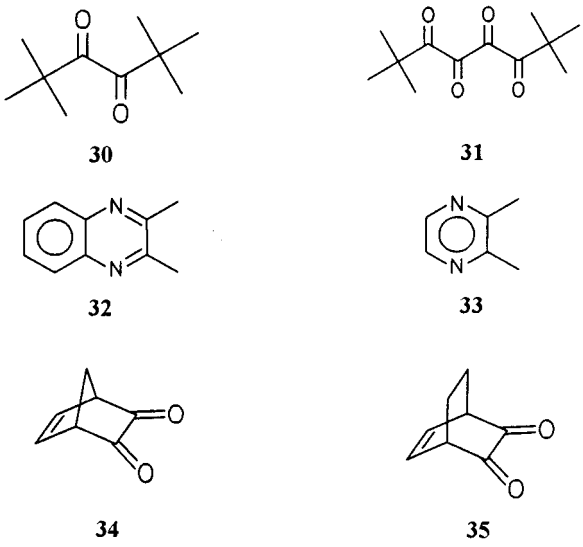
Figure 5a shows the ESR spectrum of the radical anion $\mathbf{13}^{\bullet-}$ (g = 2.0034) at 250 K generated under the same conditions. Its ^{1}H ENDOR spectrum at 220 K exhibits two couplings with a(H) = 1.16 and a(H) = 0.77 G, and general triple resonance spectroscopy reveals that both splittings have the same sign (negative). Based on these results the ESR spectrum of $\mathbf{13}^{\bullet-}$ was satisfactorily simulated with the data a(N) = 2.64 (4 N), a(H) = 1.13 (1,4,8,11-H), and a(H) = 0.69 G (2,3,9,10-H) (Figure 5a). This assignment was derived from data of corresponding quinoxaline radical anions[22]. In $\mathbf{13}^{\bullet-}$ the unpaired electron is also delocalized over the whole molecule on the ESR time scale. Accordingly, the coupling constants of $\mathbf{13}^{\bullet-}$ have about half the magnitude of the corresponding splittings reported for the 2,3-dimethylquinoxaline radical anion ($\mathbf{32}^{\bullet-}$; potassium,

Figure 5. a) ESR spectrum of the radical anion **13**$^{\bullet-}$ in DME/kryptofix® 222 at 250 K together with a simulation using a(N) = 2.64 (4 N), a(H) = 1.13 (1,4,8,11-H), and a(H) = 0.69 G (2,3,9,10-H). – b) ESR spectrum of the radical anion **17**$^{\bullet-}$ in DME/kryptofix® 222 at 250 K together with a simulation using a(N) = 3.33 (4 N) and a(H) = 1.47 G (4 H). – c) ESR spectrum of the radical anion **20**$^{\bullet-}$ in DME/kryptofix® 222 at 250 K together with a simulation using a(N) = 2.88 (4 N), a(H) = 1.17 (4 H), and a(H) = 0.73 G (4 H)



THF): a(N) = 5.13 (2 N), a(H) = 2.43 (5,8-H), a(H) = 1.40 (6,7-H), and a(H) = 2.71 G (6 H, 2,3-CH_3)[22].

Comparable results were obtained for the bicyclic bisquinoxaline-derivative radical anion **20**$^{\bullet-}$. In the ^{1}H ENDOR spectrum of **20**$^{\bullet-}$ at 200 K two weak couplings were observed corresponding to a(H) = 1.06 and a(H) = 0.76 G. The simulation of the ESR spectrum at 250 K with a(N) = 2.88 (4 N), a(H) = 1.17 (4 H), and a(H) = 0.73 G (4 H) in Figure 5c shows an acceptable agreement with experiment. In this simulation, however, no splittings due to the bridgehead and the propano-bridge hydrogens have been considered. Such splittings (see for example bicyclo[3.2.2]-nonane-2,3-dione radical anion[23][24]) could lie in the range of the observed hydrogen coupling constants, but were not clearly detected. The magnitudes of the hydrogen splittings of **20**$^{\bullet-}$, determined by ENDOR, are in accord with a delocalization of the unpaired electron over the two acceptor units on the ESR time scale.



2.2 Donor-Acceptor Systems

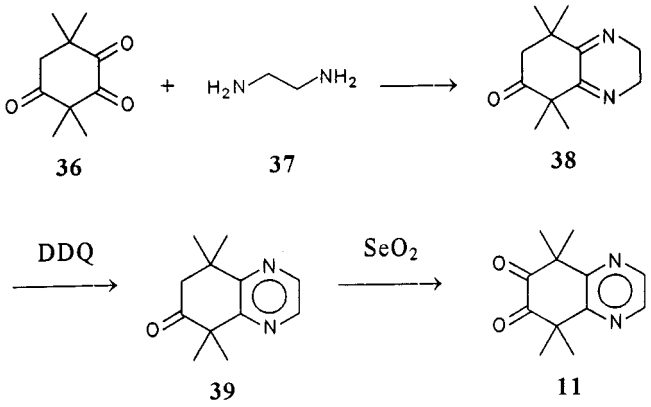
Reduction of **21** afforded readily the corresponding radical anion showing only a narrow triplet in the ESR spectra (propiophenone, potassium *tert*-butoxide in DMSO, 300 K: a(H) = 0.24 G, g = 2.0050; potassium, kryptofix® 222, DME, 220 K, ESR and ENDOR: a(H) = 0.25 G (2 H), g = 2.0050). The observed coupling constant is smaller than that in the related bicyclic species **34**$^{\bullet-}$ [a(H) = 0.73 G][25] and **35**$^{\bullet-}$ [(a(H) = 0.41 G][26]. It is interesting to note that, in contrast to **9**$^{\bullet-}$, no splitting of the methyl hydrogens could be detected in the ^{1}H ENDOR spectrum of **21**$^{\bullet-}$. The ESR spectrum of **7**$^{\bullet-}$ (potassium, kryptofix® 222, DME, 260 K) shows only one narrow line (linewidth 0.2 G) with g = 2.0051. The g-values of **7**$^{\bullet-}$ and **21**$^{\bullet-}$ are in accord with that of **9**$^{\bullet-}$.

3. Syntheses

The preparation of most of the compounds, used in our studies, were published in our ealier report on this subject[9], except for the syntheses of **11** and **14**–**16**, as well as of **23**

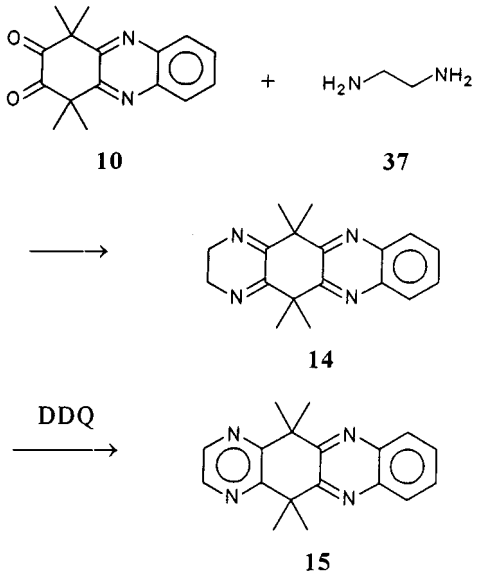
and **24**. The diketone **11** was prepared in a straight-forward way by reaction of 3,3,6,6-tetramethyl-cyclohexane-1,2,4-trione (**36**)[27] with 1,2-diaminoethane, followed by a dehydration step with DDQ and oxidation with SeO_2 (Scheme 2).

Scheme 2



The other molecules were prepared in a similar straightforward way as shown in Schemes 3−6. In the case of **24** we reduced **10** with Na in DME by applying ultrasound. The reaction product was quenched with trimethyloxonium fluoroborate to yield **24** and **43** as main components of a mixture of about five compounds.

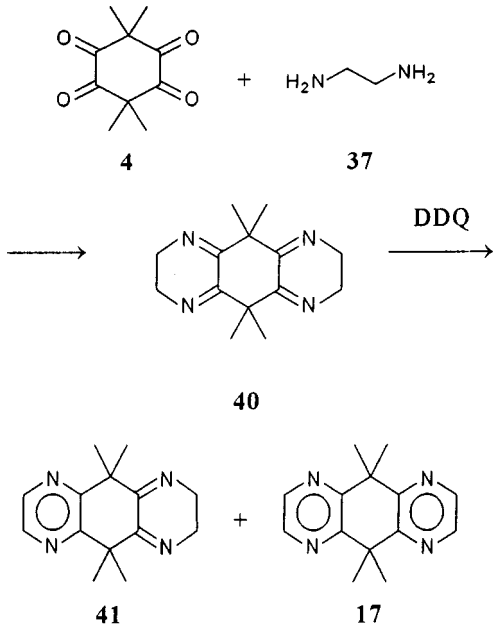
Scheme 3



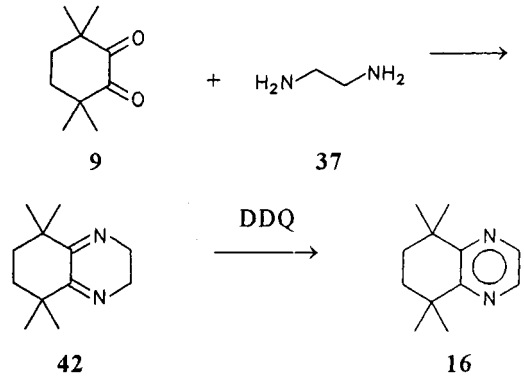
Conclusion

Our combined CV and ESR experiments of the radical anions of molecules with two acceptor groups or with one acceptor and one donor group and possible homoconjugation have shown that in the case of the radical anion of **5** and **20** delocalization of the unpaired electron over both acceptor moieties is likely. In the case of **4**, **13**, and **17** the results can best be understood on the assumption of a fast electron exchange in the radical anions. In the case of the donor-acceptor compounds both methods reveal no sign of a homoconjugation interaction in the radical anion.

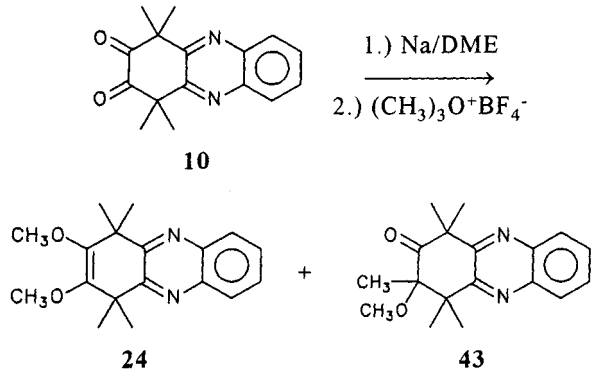
Scheme 4



Scheme 5



Scheme 6



We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *BASF Aktiengesellschaft*, *Ludwigshafen,* for financial support.

Experimental Section

ESR and ENDOR Studies: a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system was used. Determination of g values were performed using an NMR gaussmeter and a Hewlett-Packard 5342A microwave frequency counter; which was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into gauss using 1 MHz = ($0.7145/g_{ex}$) G. The radical anions were generated by reduction of the parent compounds (about 1 mg) with propiophenone and potassium *tert*-butoxide in DMSO[19] or with a potassium mirror in DME or methyltetrahydrofuran (MTHF) (1 ml) under high-vacuum conditions in the presence of kryptofix® 222 Merck (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; about 4 mg). The solvents were carefully dried (potassium) and deoxygenated. Potassium was purified by repeated vacuum destillation.

Cyclovoltammetric Measurements: The measurements were performed with a HEKA-potentiostat PG 28 using a glassy carbon disc electrode (Metrohm, 3 mm in diameter) as working electrode. A standard calomel electrode (SCE) was used as the reference electrode, and it was separated by a diaphragm and a capillary from the solution. The experiments were carried out under argon in 0.1 molar solution of tetra butylammonium-hexafluorophosphate as supporting electrolyte. Either anhydrous dimethylformamide [E_0 (Fe/Fe^+ = 480 mV)] or anhydrous methylenechloride [E_0 (Fe/Fe^+ 420 mV)] was used as solvent. The same scan rates were employed for both solvents.

2,3,5,6,7,8-Hexahydro-5,5,8,8-tetramethylquinoxaline-6-one (**38**): To a solution of 525 mg (2.86 mmol) of 3,3,6,6-tetramethylcyclohexane-1,2,4-trione (**36**)[27] in 150 ml of anhydrous toluene were added 173 mg (2.88 mmol) of anhydrous 1,2-diaminoethane. The mixture was refluxed for 45 min, cooled, and chromatographed (silica gel, petroleum ether/diethylether, 0.5:1) after removal of the solvent under reduced pressure. The resulting product was further purified by Kugelrohr distillation at 130°C (0.5 mbar) to yield 286 mg (49%) of **38** as slightly yellow crystals; m.p. 68−69°C. − IR ($CDCl_3$): ν = 2950 cm^{-1}, 2926, 2862, 2840, 2216, 1709, 1587, 1433. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.37 (s, 4 H), 2.64 (s, 2 H), 1.29 (s, 6 H), 1.13 (s, 6 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 210.43, 165.16, 164.70, 53.31, 50.50, 45.21, 44.95, 38.51, 26.61, 24.50. − $C_{12}H_{18}N_2O$ (206.3): calcd. C 69.87, H 8.79, N 13.58; found C 69.77, H 8.60, N 13.44.

5,6,7,8-Tetrahydro-5,5,8,8-tetramethylquinoxaline-6-one (**39**): A solution of 730 mg (3.54 mmol) of **38** and 890 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (3.92 mmol) in 150 ml of anhydrous toluene was refluxed for 3 h. After cooling the solution, the precipitated hydroquinone-derivative was filtered off. Purification by silica gel chromatography (petroleum ether/diethylether, 1:1) and subsequent Kugelrohr distillation at 110°C/0.06 mbar yielded 616 mg (85%) of **39** as colorless crystals, m.p. 37−38°C. − IR ($CDCl_3$): ν = 3036 cm^{-1}, 2984, 2952, 2924, 2860, 2222, 1706, 1440, 1418. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.44 (d, *J* = 2.3 Hz, 1 H), 8.40 (d, *J* = 2.3 Hz, 1 H), 2.73, (s, 2 H), 1.45 (s, 6 H), 1.32 (s, 6 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 211.57, 156.96, 156.16, 142.73, 141.93, 50.76, 50.62, 38.25, 28.58, 26.35. − $C_{12}H_{16}N_2O$ (204.3): calcd. C 70.56, H 7.89, N 13.71; found C70.57, H 7.82, N 13.53.

5,6,7,8-Tetrahydro-5,5,8,8-tetramethylquinoxaline-6,7-dione (**11**): A mixture of 100 mg (0.49 mmol) of **39** and 61 mg (0.55 mmol) of selenium dioxide was refluxed in 10 ml of anhydrous toluene for 16 h. The solution was cooled, the precipitated selenium was filtered off, and the solvent was removed under reduced pressure. The residue was purified by Kugelrohr distillation at 130°C/0.06 mbar and yielded 35 mg (33%) of **11** as yellow crystals, m.p. 122−123°C. − IR ($CDCl_3$): ν = 3042 cm^{-1}, 2962, 2928, 2864, 1723, 1401, 1146. − UV/Vis (CH_2Cl_2): λ max (ε) = 404 nm (28), 318 (982), 274 (72000). − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.54 (s, 2 H), 1.56 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 202.61, 153.47, 143.76, 52.19, 24.83. − HRMS/EI, $C_{12}H_{14}N_2O$: calcd. 218.1055, found 218.1063.

2,3,5,12-Tetrahydro-5,5,12,12-tetramethylpyrazino[2,3-b]phenazine (**14**) *and 5,12-Dihydro-5,5,12,12-tetramethylpyrazino[2,3-b]-phenazine* (**15**): A mixture of 200 mg (0.75 mmol) of **10**[9] and 52 mg (0.87 mmol) of 1,2-diaminoethane (**37**) was refluxed for 3 h in 25 ml of anhydrous toluene. The work up procedure was the same as for **38**. Kugelrohr distillation at 160°C/ 0.05 mbar yielded 118 mg (54%) of **14** as colorless crystals, m.p. 173−175°C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.07−8.01 (m, 2 H), 7.71−7.66 (m, 2 H), 3.46 (s, 4 H), 1.66 (s, 12 H). − ^{13}C NMR($CDCl_3$, 75.46 MHz): δ = 164.92, 155.71, 141.65, 129.27, 128.89, 45.79, 45.38, 28.68. − $C_{18}H_{20}N_4$ (292.4): calcd. C 73.94, H 6.89, N 19.16, found C 73.73, H 6.90, N 18.89.

15: A mixture of 81 mg (0.28 mmol) of **14** and 70 mg (0.31 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was refluxed for 4 h in 30 ml of anhydrous toluene. After cooling the preciptated hydroquinone derivative was filtered off. The solution was chromatographed on silica gel with petroleumether/diethylether (2.5:1) as eluent. The product was further purified by Kugelrohr distillation and yielded 45 mg (54%) of **15** as colorless crystals m.p. 157−158°C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.57 (s, 2 H), 8.12−8.07 (m, 2 H), 7.74−7.68 (m, 2 H), 1.86 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 155.71, 154.83, 142.90, 141.85, 129.22, 128.92, 43.87, 31.01. − UV/Vis (CH_2Cl_2): λ max (ε) = 324 nm (13000), 316 (10500), 280 (119000), 274 (11900), 240 (27500). − $C_{18}H_{18}N_4$ (290.4): calcd. C 74.46, H 6.25, N 19.30, found C 74.64, H 6.31, N 19.04.

2,3,5,7,8,10-Hexahydro-5,5,10,10-tetramethylpyrazino[2,3-g]-quinoxaline (**40**): A solution of 2.0 g (10.2 mmol) of **4**[27] in 330 ml of anhydrous toluene was heated until the tetraketone was dissolved. To the yellow solution was added 1.23 g (20.4 mmol) of 1,2-diaminoethane in 30 ml of toluene over the course of 30 minutes. After the addition was completed, the mixture was refluxed for 1 h and stirred at room temperature for 18 h. The solution was then chromatographed on silica gel with diethylether as eluent. The crude product was purified by sublimation and yielded 1.11g (47%) of **40** as colorless crystals, m.p. 119°C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.37 (s, 8 H), 1.33 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 164.33, 47.94, 45.30, 25.74. − $C_{14}H_{20}N_2$ (244.3): calcd. C68.82, H 8.25, N 22.93; found C69.00, H 8.43, N 22.84.

5,10-Dihydro-5,5,10,10-tetramethylpyrazino[2,3-g]quinoxaline (**17**) *and 2,3,5,10-Tetrahydro-5,5,10,10-tetramethylpyrazino[2,3-g]quinoxaline* (**41**): A solution of 300 mg **40** (1.23 mmol) and 419 mg of DDQ (1.23 mmol) in 150 ml of toluene was refluxed for 3.5 h.The work up was the same as described for **39**. The chromatography yielded **17** and **41**. Both compounds were purified by sublimation in a Kugelrohr apparatus to yield 14 mg (5%) of **41** and 184 mg (63%) of **17**. − **41**: pale yellow crystals, m.p. 102−103°C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.47 (s, 2 H), 3.43 (s, 4 H), 1.54 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 164.68, 154.86, 142.74, 45.29, 44.72, 28.34. − $C_{14}H_{18}N_4$ (242.3): calcd. C 69.39, H 7.49, N 23.12; found C69.42, H 7.45, N 22.83. − **17**: colorless crystals, m.p. 172−173°C. − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.23 (s, 4 H), 1.72 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 154.63, 142.89, 42.87, 30.66. − $C_{14}H_{16}N_4$ (240.3): calcd. C 69.97, H 6.71, N 23.31; found C 69.97, H 6.70, N 23.30.

2,3,5,6,7,8-Hexahydro-5,5,8,8-tetramethylquinoxaline (**42**): A solution of 200 mg (1.19 mmol) of 3,3,6,6-tetramethylcyclohexan-1,2-dione (**9**)[28] and 79 mg (1.31 mmol) of 1,2-diaminoethane in toluene was refluxed for 3 h. The work up procedure was the same as that in the preparation of **38**. The resulting product was further purified by Kugelrohr distillation, yielding 180 mg (79%) of **42** as colorless solid, m.p. 30−31°C. − ^{1}H NMR($CDCl_3$, 300 MHz): δ = 3.16 (s, 4 H), 1.66 (s, 4 H), 1.05 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 167.68, 45.05, 39.54, 34.16, 26.61. − $C_{12}H_{20}N_2$ (192.3): calcd. C 74.95, H 10.48, N 14.57; found C 74.94, H 10.42, N 14.37.

5,6,7,8-Tetrahydro-5,5,8,8-tetramethylquinoxaline (**16**): A solution of 55 mg (0.27 mmol) of **42** and 73 mg (0.32 mmol) of DDQ in 25 ml of toluene was refluxed for 3 h. The work-up was the same as described for **39**. After column chromatography the product was purified by Kugelrohr distillation at 140°C/ 3 mbar which yielded 39 mg (76%) of a colorless solid, m.p. 25°C. − ^{1}H NMR($CDCl_3$, 300 MHz): δ = 8.32 (s, 2 H), 1.77 (s, 4 H), 1.30 (s, 12 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 158.68, 141.43, 37.10, 34.03, 29.74. − $C_{12}H_{18}N_2$ (190.3): calcd. C 75.74, H 9.53, N 14.72; found C 75.49, H 9.62, N 14.53.

Reduction of 1,2,3,4-Tetrahydro-1,1,4,4-tetramethylphenazine-2,3-dione (**10**) *with Na:* The reaction was carried out in a Schlenk-tube under argon with anhydrous, oxygen-free solvents. A solution of 106 mg (40 mmol) of **10**[9] in 5 ml of anhydrous 1,2-dimethoxyethane and 40 mg (1.74 mmol) of sodium was treated for 5 h with ultrasound. When most of the sodium had disappeared 250 mg (1.69 mmol) of trimethyloxonium tetrafluoroborate was added. After a few more minutes of treatment of the solution with ultrasound, the dark solution changed color into yellow. The solution was than filtered (silica gel) and the solvent removed under reduced pressure. Purification was achieved by preparative thin-layer chromatography, which yielded 13 mg (11%) of 1,4-dihydro-2,3-dimethoxy-1,1,4,4-tetramethylphenazine (**24**) and 64 mg (28%) 2-methoxy-1,1,2,4,4-pentamethyl-1,2,3,4-tetrahydrophenazine-3-one (**43**), both as colorless crystals. Three other products in small amounts (5−10 mg) could not be purified completely. − **24**: m.p. 120−122°C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.05−8.01 (m, 2 H), 7.70−7.66 (m, 2 H), 3.82 (s, 6 H), 1.57 (s, 12 H). − ^{13}C NMR($CDCl_3$, 75.46 MHz): δ = 156.44, 144.39, 142.55, 128.88, 128,78, 59.96, 42.31, 27.85. − HRMS/EI, $C_{18}H_{22}N_2O_2$: calcd. 298.1681, found 298.1735. − **43**: m.p. 124−125°C. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.05−7.99 (m, 2 H), 7.69−7.63 (m, 2 H), 3.11 (s, 3 H), 1.72 (s, 3 H), 1.65 (s, 3 H), 1.58 (s, 3 H), 1.42 (s, 3 H), 1.14 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ = 212.50, 157.31, 156.94, 141.34, 140.92, 128.90, 128.78, 128.76, 128.53, 85.00, 52.74, 49.31, 46.28, 28.45, 28.14, 25.60, 19.65, 11.96. − $C_{18}H_{22}N_2O_2$ (298.4): calcd. C 72.46; H 7.43, N 9.53; found C 72.63, H 7.50, N 9.30.

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