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Structural and Chemical Properties of 1,2-Bis(*N*-methyl-4-pyridyl)ethylene

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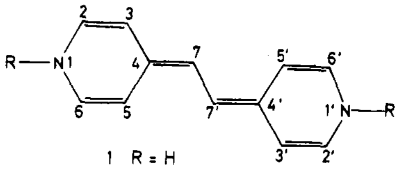
The nonconjugated pyridinyl diradicals of the type Py•–$(CH_2)_n$–Py• (n = 2–4) provide significant information regarding intramolecular spin–spin interaction between two π-radical moieties in a molecule.[1] In this connection, 1,2-bis(4-pyridyl)ethylene (**1**) and its higher homologues are intriguing, provided that they assume a so-called diradical structure corresponding to a resonance form given by Py•–(CH=CH)$_n$–Py• in the ground state. About two decades ago, Happ et al.[2] have attempted to prepare 1,2-bis(*N*-methyl-4-pyridyl)ethylene (**2**) by two-electron reduction of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate (**3**) under oxygen-free nitrogen. From the visible absorption and EPR spectroscopy, the product was assigned to the neutral, doubly reduced species **2**. Since then, however, no definite information has been reported about the product.[3] Thus it seems that there is still much room for raising questions about the assignment. With this background, we decided to prepare **2** by two-electron reduction of 1,2-bis(*N*-methyl-4-pyridyl)ethylene dibromide (**4**) with sodium amalgam under vacuum of 10^{-6} Torr. It is shown that the present product is clearly characterized by means of NMR, EPR, and UV-vis absorption spectroscopy and of semiempirical MO calculations.[4,5] It is also made clear that the product prepared previously under oxygen-free nitrogen should be a mixture of several decomposition products generated from **2** by oxidative reactions.[6]



1 R = H
2 R = CH_3

Results and Discussion

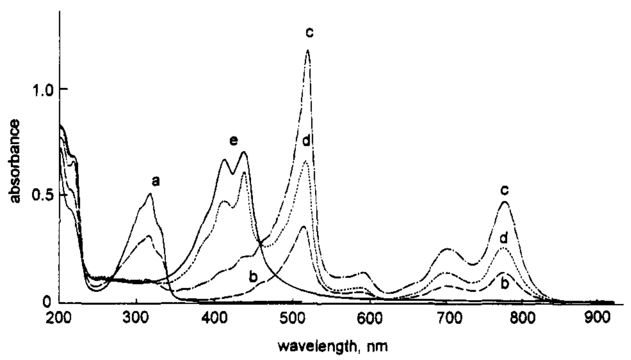


Figure 1. Absorption spectral change during the course of reduction of **4** with 3% sodium amalgam in CH_3CN at 0 °C: (a) before reduction, (b) after 0.25 h, (c) after 3 h, (d) after 4 h, and (e) after 8 h.

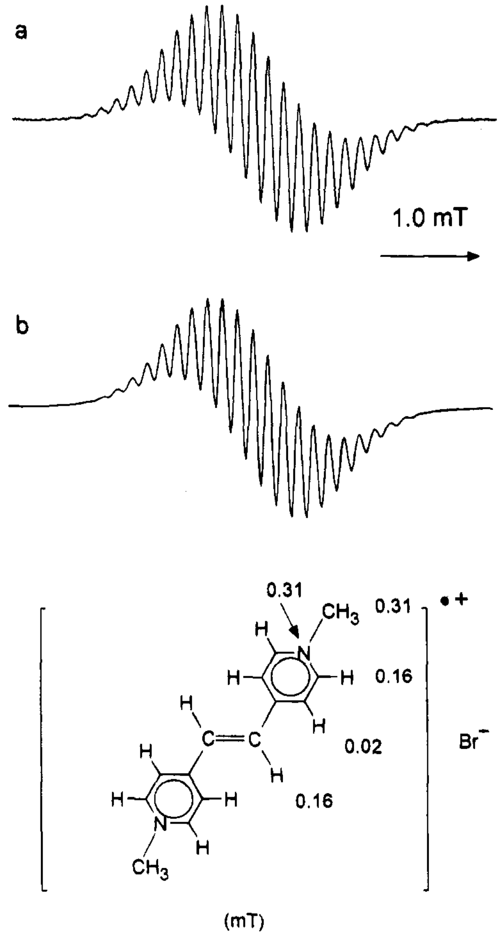


Figure 2. EPR spectrum of **5** in CH_3CN at rt and hfs constants in mT: (a) measured and (b) simulated.

Preparation of 2. Reduction of **4** with sodium amalgam in degassed acetonitrile was followed by means of UV-vis absorption spectroscopy. Figure 1 shows the spectral change during the course of reduction, where the spectral line (a) corresponds to the spectrum of **4**. After about 3 h the absorption spectrum changes into the spectral line (c). This spectral feature resembles the spectrum of the cation radical of **3** reported previously.[2] The solution of this stage has a deep purple color, exhibiting a strong EPR spectrum as shown in Figure 2a. The hfs constants obtained by means of a computer simulation (Figure 2b) are almost in agreement with the reported values by Happ et al.[2] The 1,2-bis(*N*-methyl-4-pyridyl)ethylene bromide cation radical (**5**) thus prepared is stable for a long period of time in Na–Hg free

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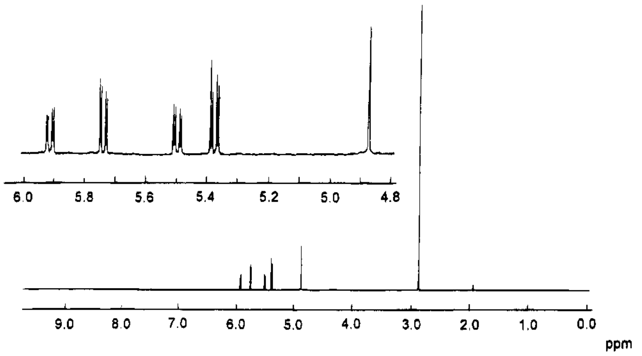

Figure 3. ^{1}H NMR spectrum of **2** in CD_3CN at rt.

solution at room temperature. After further reduction the solution changes gradually from purple to reddish yellow, and after about 8 h the absorption spectrum changes into the spectral line (e). At this stage of reduction, the solution shows no EPR signal at all, indicating the formation of diamagnetic species. As a result, these spectral changes with elapse of time indicate that **4** undergoes clearly two-stage one-electron reduction. Noteworthily, the absorption spectrum (e) of the doubly reduced product differs markedly in shape from that observed by Happ et al. An explanation for this difference can be offered below.

Characterization and Properties of 2. Figure 3 shows the ^{1}H NMR spectrum of 2. Inspection of the spectrum reveals that the four well separated bands at the region of 5.38–5.92 ppm can be assigned as arising from the protons of two pyridine rings. The proton signal at 4.88 ppm, which is specific to those of olefinic compounds, is assigned to H7(H7′) attached to the exocyclic C atoms. The ^{13}C NMR spectrum indicates that the five signals at 106.4, 114.4, 126.1, 130.6, and 133.2 ppm are assigned to C3(C3′), C5(C5′), C4(C4′), C6(C6′), and C2(C2′) of pyridine rings and the signal at 102.0 ppm to the exocyclic C7(C7′) with sp^2 configuration. The correlation between the protons and the C atoms can be made clear by the C,H-COSY spectrum shown in Figure 4. Namely, each peak of the ^{13}C NMR spectrum is assigned to the respective peak of ^{1}H NMR spectrum by picking out the cross peak. The ^{1}H and ^{13}C NMR spectral data are summarized in Table 1 together with their assignments. As a consequence, the present reduction product is identified as the desired compound **2**,[7] in which two pyridylidene skeletons are conjugated with each other via the exocyclic C atoms.

Table 1. ^{1}H and ^{13}C NMR Spectral Data of 2 in CD_3CN[a]

position	^{1}H NMR δ (ppm)	*J* (Hz)	^{13}C NMR δ (ppm)
2,2′	5.92 (dd)[b]	7.81, 1.96	133.24
3,3′	5.50 (dd)	7.81, 2.44	106.38
4,4′			126.09
5,5′	5.38 (dd)	7.81, 2.44	114.42
6,6′	5.74 (dd)	7.81, 1.96	130.64
7,7′	4.88 (s)		102.04
CH_3	2.87 (s)		40.26

[a] ^{1}H and ^{13}C NMR chemical shifts were recorded with reference to CD_3CN: ^{1}H NMR, 1.94 ppm; ^{13}C NMR, 117.7 ppm. [b] s = singlet and dd = double-doublet.

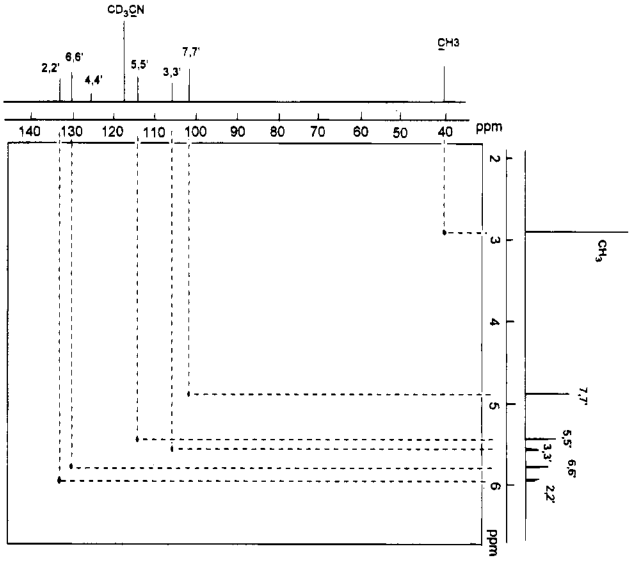

Figure 4. H,C-COSY spectrum of **2** in CD_3CN at rt.

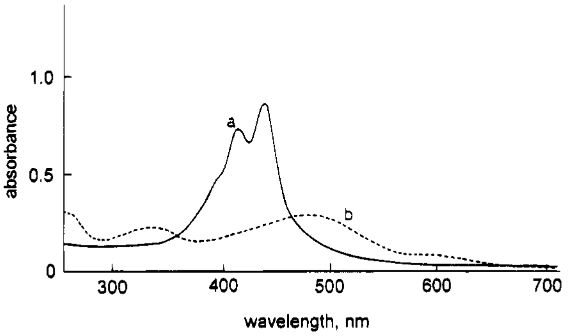

Figure 5. Absorption spectra in CH_3CN: (a) **2** and (b) its oxidative decomposition products.

It is noted that no modifications of the NMR and absorption spectra are observed at all by warming **2** for many hours in MTHF or in acetonitrile at 80 °C in vacuo. Further, neither an EPR signal nor an absorption spectral change is observed by light irradiation on **2** in MTHF at −196 °C. This indicates that under the absence of air oxygen, **2** is insensitive to heat and light and hence a highly stable species. In marked contrast, **2** is very reactive under the presence of air oxygen. That is, **2** decomposes readily to give several degradation products when exposed to air or in an atmosphere of oxygen-free nitrogen. This is confirmed by means of NMR spectroscopy, which reveals that the ^{1}H NMR signals characteristic of **2** disappear completely and new complex signals appear over the wide range of chemical shifts, 1.7–9.1 ppm. At the same time, the resulting solution exhibits a broad absorption band over the range of wavelengths, 400–500 nm, and a weak absorption band at the region of 610 nm (Figure 5). Noticeably, this spectral feature resembles quite well the spectrum observed by Happ et al. From the facts we can safely say that the reduction product prepared previously under oxygen-free nitrogen should be in fact a mixture of several degradation products generated from **2** by oxidative reactions.[6]

Molecular Orbital Treatments of 2. To gain the structural information on **2**, we carried out the molecular structure calculations by means of the MNDO MO method[4] and by assuming a planar trans-structure of C_2 symmetry. The MNDO full geometry optimization of **2**

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(7) When 1 equiv of **4** is added to 1 equiv of **2** in CH_3CN, the solution changes from orange to purple. The EPR spectrum for this solution is the same as that of **5** prepared by one-electron reduction of **4**. This shows that **2** is produced in the reversible redox process given by $\mathbf{2} + \mathbf{4} \rightleftharpoons \mathbf{5}$. This evidence lends further support for the structural assignment for **2**.

Table 2. Calculated Singlet Transition Energies and Intensities of 1

compound	transition symmetry	theoretical ΔE (eV)	theoretical f (cgs)	experimental[a] ΔE (eV)
1[b]	B	3.062	2.083	2.844, 3.009
	A	3.186	0	
	B	3.193	0.012	3.204, 3.415
	A	4.192	0	4.444
	A	4.934	0	4.843
	B	5.698	0.053	5.793
	A	5.699	0	

[a] The spectrum of **2** in CH_3CN. [b] The molecular symmetry group of **1** is assumed to be of C_2 symmetry.

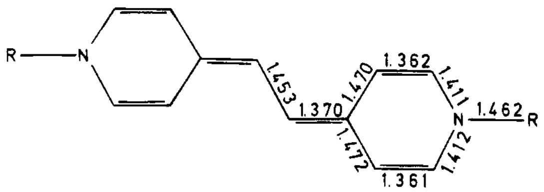

Figure 6. Optimized bond lengths (Å) of **2**.

arrives at a nuclear arrangement consisting of two pyridylidene moieties as the favored structure. This indicates that **2** should definitely possess a singlet ground state instead of a triplet diradical. The heat of formation is calculated to be 95.97 kcal/mol. Figure 6 shows bond lengths (Å) for the optimized geometrical structure of **2**. Since a marked bond fixation is observed on the molecular skeleton, **2** can be regarded as being a nonaromatic polyene. This may be correlated to the experimental fact that **2** is readily oxidized to give degradation products.

To discuss the excited states of **2**, we carried out UV-vis spectroscopic calculations of **1** by using the PPP-type SCF MO CI method.[5] Here configuration mixing of all the singly excited states is included. In Table 2 are presented the calculated transition energies and intensities of **1** for comparison with the available experimental data. It is predicted that **1** has a strong absorption band at 3.06 eV. Thus the strong absorption peak at 2.84 eV of **2** is assigned to the allowed transition of B symmetry, and the peak at 3.01 eV is interpreted as being a vibrational structure of the electronic excited state. One additional transition at a shorter wavelength than that of the strong transition is predicted, but the oscillator strength is less than that of the strong transition. This suggests that the weak absorption peaks at 3.20 and 3.42 eV should be assigned to the second allowed transition of B symmetry. Moreover, the strong absorption peak at 5.79 eV is assigned to the third allowed transition of B symmetry. It is thus seen that the observed absorption peaks can be well accounted for by using the predicted singlet transitions of **1**. In this connection, we further refer to the lower excited triplet states of **2**. The triplet CI calculations of **1** lead to the prediction that the first and second excited triplet states lie above the ground state by 0.56 and 1.69 eV, respectively. Since the first excited triplet state is predicted to lie in the infrared region, the high reactivity of **2** under air oxygen may be ascribed to the existence of such a lower lying triplet state.

Conclusion

Compound **2** was prepared by two-electron reduction of **4** with sodium amalgam in vacuo and characterized by means of NMR, EPR, and UV-vis absorption spectroscopy and of the semiempirical MO calculations. It was found that in the presence of air oxygen **2** is highly reactive, decomposing readily to give several degradation products. This behavior is accounted for by the theoretical findings that **2** should take a nonaromatic polyene structure with a marked bond fixation and possess a lower lying triplet state easily accessible thermally.

Experimental Section

General. Standard vacuum line techniques were used in the preparation of **2**, **5**, and solvents. UV-vis spectra were measured on a Hitachi H220S spectrophotometer, the EPR spectrum was recorded on a Bruker ESP300E EPR spectrometer, and NMR spectra were recorded on a JNM-EXE400 NMR spectrometer. The 2D H,C-COSY technique was used to analyze ^1H and ^{13}C NMR spectra of **2**. To examine the course of reduction spectroscopically, the reaction flask was equipped with cells for EPR and absorption spectral measurements connected with/through an intervening sintered glass filter. During the reduction, both spectra were measured periodically after filtration.

Material. A solution of **4** was prepared by treating 1,2-dipyridylethylene with a large excess of methyl bromide in methanol in a tube at 0 °C for about 60 h. A solid product was separated by filtration and recrystallized from methanol to yield colorless crystals, mp 250–254 °C. Anal. Found: C, 45.50; H, 4.25; N, 7.72. Calcd for $C_{14}H_{16}N_2Br_2$: C, 45.41; H, 4.36; N, 7.57%.

Solvents. Acetonitrile (Guaranteed Reagent) was passed through an alumina column and distilled. After degassing, the solvent was treated with 1-methyl-4-(methoxycarbonyl)pyridinyl radical to remove radical-reactive impurities. MTHF was refluxed over sodium for 3 days, degassed, and then distilled onto sodium and anthracene in a storage vessel.

Reduction of 4. In a reaction flask connected to a vacuum line were placed **4** (1.3×10^{-2} mmol), 3% sodium amalgam (5.2×10^{-2} mmol), and a Teflon-sealed stirring bar. After 6 h of pumping at 10^{-6} Torr, degassed acetonitrile (30 mL) was distilled in, and the flask was sealed and stirred at 0 °C. With progressive reduction the solution became purple, and by further reduction the solution changed gradually to reddish yellow. After about 8 h, the solvent was removed, and the residue was extracted with MTHF to obtain the solution containing the resulting reduction product.

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