Chem. Ber. 113, 2049 – 2051 (1980)

Verdazyls, 27[1)]

1,1',5,5'-Tetraphenyl-3,3'-biverdazyl, the Primary Bisverdazyl

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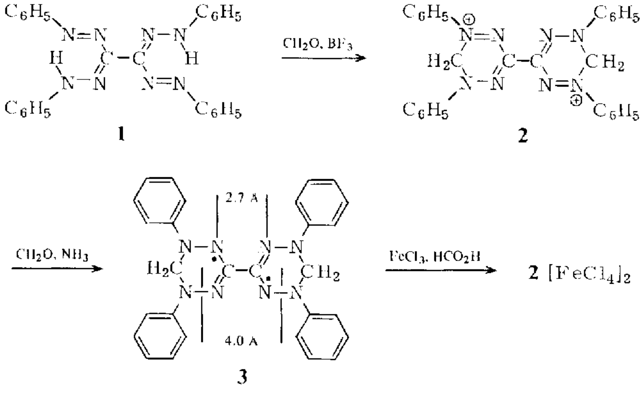
Received November 28, 1979

Verdazyle, 27[1)]

1,1',5,5'-Tetraphenyl-3,3'-biverdazyl, das primäre Bisverdazyl

Die Titelverbindung 3 wurde dargestellt. Die gefundenen Nullfeldaufspaltungsparameter $|D'| = 305$ G und $|E'| \approx 0$ G entsprechen der Struktur.

In our bisverdazyl studies[2,3)] the primary bisverdazyl **3** has always been an object of considerable interest, particularly in connection with the application of bisverdazyls as biradical spin probes[4)]. As a consequence of its large zero field splitting parameter D' **3** is expected to show triplet satellites, non-overlapping with monoverdazyl signals in the ESR spectrum. The formation of monoradicals can hardly be avoided in biradical spin probe studies. Our attempts, however, failed to obtain **3** from the corresponding bisformazan (diformazyl)[5)] by conventional methods. The re-examination of the starting material revealed, that "diformazyl" has in fact another constitution[6)]. Lately we succeeded in synthesizing the required bisformazan **1**, which turned out to be a thermolabile compound[7)].



Reaction of **1** with formaldehyde in the presence of $BF_3 \cdot Et_2O$ yielded the bisverdazylium ion **2**, which was subsequently reduced to the bisverdazyl **3** under basic conditions. **2** was characterized as $FeCl_4$ salt.

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In contrast to other C-3,C-3'-linked bisverdazyls[2] **3** is not a stable compound. Although it can be isolated as nice black crystals, the purity of the bisverdazyl did not exceed 90% (checked by microhydrogenation in combination with absorption spectra). IR spectra indicate the presence of some leucoverdazyl (3340 cm^{-1}, νNH). ESR spectra show the hyperfine structure signals of monoverdazyl besides the triplet satellites. At room temperature **3** decomposes almost quantitatively within few days, and also at lower temperatures a continuous decrease of the biradical concentration is observed.

The triplet state of **3** is clearly shown by its ESR spectra taken in rigid glasses of either dimethylformamide or toluene (Figure) at 88 K. The experimental spectrum is dominated by a large splitting arising from randomly oriented triplets. Computer simulation was achieved with a FORTRAN program for line shape calculations of triplets[8]. A set of zero field splitting parameters $|D'| = 305$ G and $|E'| \approx 0$ G shows the zero field splitting tensor to be axially symmetric within the experimental error. The unusual large line width parameter $HB = 80$ G used in the calculation may reflect several conformations of **3** with slightly differing zero field parameters.

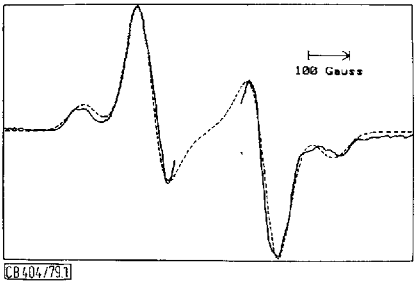

Fig. Experimental (———) and simulated (– – –) ESR spectrum of **3** in toluene at 88 K. Signals due to monoradical in the center of the experimental spectrum have been omitted. Simulation was obtained with $|D'| = 305$ G, $|E'| = 0$ G and Gaussian line shape with a line width parameter $HB = 80$ G

The observed $|D'| = 305$ G can be converted into a hypothetical average distance r between the two unpaired electrons using the two point model $|D'| = 3g\mu_B/3r^3$. The resulting distance $r = 3.57$ Å agrees almost with the distance between the midpoints of both verdazyl rings corresponding to the expectation. In the verdazyl system most of the spin density is nearly equally distributed among the four nitrogens. The indicated distances in the formula are estimated from x-ray structure analysis data of 1,3,5-triphenylverdazyl[9].

Due to its instability the primary bisverdazyl **3** can hardly be used as a biradical spin probe. Furthermore the ESR studies of **3** in nematic phase N9 (Merck) show, that the direct C-3,C-3'-linkage of verdazyl units leads to a significant decrease of the molecular anisotropy as compared to the spin probe 1,4-bis(1,5-diphenylverdazyl-3-yl)benzene[4].

We thank the *Deutsche Forschungsgemeinschaft* for the support of our work.

Experimental Part

1,1',5,5'-Tetraphenyl-3,3'-biverdazyl (**3**): The mixture of 1.0 g paraformaldehyde and 5 ml BF_3 ethyl etherate in 80 ml methylene chloride was stirred for 10 min. Then the filtered solution was added to 5.0 g 1,1',5,5'-tetraphenyl-3,3'-biformazan (**1**) dissolved in 10 ml methylene chloride. After stirring for 8 h at room temperature the dark solid product was collected and washed with diethyl ether. To the solution of this salt in 20 ml dimethylformamide we added 1 ml 38% aqueous formaldehyde and then ≈ 50 ml 1 N ammonia. The separated green product was filtered off and chromatographed on Al_2O_3 (Brockmann), using methylene chloride containing 0.1% triethylamine as eluent, to yield from benzene or dimethylformamide 0.6 g (11%) black crystals, m. p. 126 – 128 °C (dec.). – UV-VIS (dimethylformamide): λ_{max} (lg ε) = 686 nm (3.91).

$C_{28}H_{24}N_8$ (472.5) Calc. C 71.16 H 5.12 N 23.72 Found C 71.20 H 5.22 N 23.93

1,1',5,5'-Tetraphenyl-3,3'-biverdazylium · 2 FeCl$_4$ (**2** · 2 $FeCl_4$): To the solution of 40 mg **3** in 2 ml formic acid we added a solution of 50 mg $FeCl_3$ in 1 ml formic acid. After standing for 5 h the formed product was filtered off, washed with diethyl ether and dried to give 55 mg (75%) almost black crystals, m. p. 197 – 198 °C (dec.) – UV-VIS (HCO_2H): λ_{max} (lg ε) = 535 (4.43), 347 nm (4.60).

$C_{28}H_{24}Cl_8Fe_2N_8$ (867.8) Calc. C 38.74 H 2.79 N 12.91 Found C 38.73 H 2.83 N 12.73

References

[1] Verdazyls, 26: *F. A. Neugebauer* and *H. Fischer,* Tetrahedron Lett. **1977**, 3345.

[2] *R. Kuhn, F. A. Neugebauer,* and *H. Trischmann,* Monatsh. Chem. **97**, 525 (1966).

[3] *F. A. Neugebauer, R. Bernhardt,* and *H. Fischer,* Chem. Ber. **110**, 2254 (1977).

[4] *G. Kothe,* Nachr. Chem. Tech. Lab. **26**, 211 (1978).

[5] *E. Bamberger* and *J. Müller,* J. Prakt. Chem. **64**, 199 (1911); *E. Bamberger* and *F. Kuhlemann,* Ber. Dtsch. Chem. Ges. **26**, 2978 (1893); *I. Hausser, D. Jerchel,* and *R. Kuhn,* Chem. Ber. **82**, 515 (1949); *D. Jerchel* and *H. Fischer,* Liebigs Ann. Chem. **563**, 208 (1949).

[6] *F. A. Neugebauer, H. Fischer,* and *C. Krieger,* Chem. Ber. **112**, 2369 (1979).

[7] *F. A. Neugebauer* and *H. Fischer,* Chem. Ber. **113**, 1226 (1980).

[8] *E. Ohmes* and *G. Kothe,* unpublished.

[9] *D. E. Williams,* J. Am. Chem. Soc. **91**, 1243 (1969).

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