Oligo(1,4-phenylenepyrazole-3,5-diyl)s

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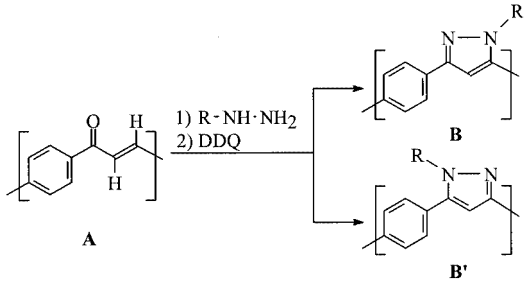
The bifunctional nucleophile methylhydrazine reacts in an alkaline medium in a regioselective mode with chalcones to yield 2-pyrazolines, which can be oxidized by DDQ to the corresponding 1*H*-pyrazoles. From oligo(chalcone)s this reaction yields cross-conjugated compounds with an alternating sequence of 1,4-disubstituted benzene rings and 3,5-disubstituted 1*H*-pyrazole rings.

Introduction

Conjugated or cross-conjugated oligomers, which consist of arylene or hetarylene building blocks, represent an area of wide current interest in organic synthesis and materials science.[1] Some time ago we reported on oligo(chalcone)s[2−4] and their transformation to oligo(*p*-phenylene-*m*-pyridinediyl)s.[5] The enone substructure is suitable for the generation of heterocycles with five-, six- and seven-membered rings.[6] We have now studied the formation of 1,4-phenylene-3,5−1*H*-pyrazolediyl units **B** from 1,4-phenylene-1,3-propenoylene units **A** in oligomers. Scheme 1 illustrates that the reaction with hydrazine derivatives and subsequent oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone can principally lead to regioisomers **B** and **B′**. Only for R = H, does a fast tautomeric equilibrium **B** ⥋ **B′** exist.



Scheme 1. Formation of phenylene-1*H*-pyrazolediyl repeat units from chalcone building blocks

Results and Discussion

There are several methods in the literature for the transformation of enones with hydrazines to pyrazolines and further to 1*H*-pyrazoles.[7−19] Very recently, Silva, Elguero and co-workers reported on a route that is based on dibromo adducts of the enones.[20] Since α,β-unsaturated ketones are bifunctional electrophiles and monosubstituted hydrazines are unsymmetric bifunctional nucleophiles, there are altogether four possibilities for the initial attack, forming two isomeric 1*H*-pyrazoles as a result (Scheme 1). The selectivity of the process depends on the steric and electronic effects of the two components and on the reaction conditions[8,10,11,13,15], the latter influencing particularly the reversion of the regioselectivity.[8] The often discussed alternative between 1,2- and 1,4-addition[10,13,15] is somewhat misleading; we suggest in Scheme 2 that in an alkaline medium N-1 of methylhydrazine (**2**) attacks C-3 of the enone. Thus, a stabilized anion **3** is generated which cyclizes to the 2-pyrazoline **4**. In the protic solvent methanol the process is more complicated. Apart from the Michael-type addition **1′** + **2** → **3′**, the intermediate formation of an *N*-methylhydrazone **3′′** can take place. Cyclization then again leads to **4** which is oxidized by DDQ to the 1*H*-pyrazole **6**. Monitoring the reaction by ^{1}H NMR spectroscopy in CD_3OD revealed that after the addition of **1** and **2** a new olefinic AB system is formed with a $^3J_{trans}$ coupling constant of 16.3 Hz, which we attribute to **3′′**. Since at least three NCH_3 singlet signals can be observed, which do not belong to **2** or **4**, we assume, that the reaction route **1′** + **2** → **3′** → **4** competes with the reaction route **1′** + **2** → **3′′** → **4**.

The same procedures, applied to enone **7**, gave the 1*H*-pyrazole **9** via the 2-pyrazoline **8** (Scheme 3). The yields are generally somewhat higher for alkaline catalysis than for the reaction in methanol.

After these primary experiments, we were surprised by the reactivity of the bis(chalcone) **10**. The variant in methanol yielded, after oxidation, compounds **11** and **12** in a ratio of 46:54. In contrast to the chalcones **1** and **7**, one enone unit of **10** can react with the opposite regioselectivity. Moreover, the structure of the major product **12** differs

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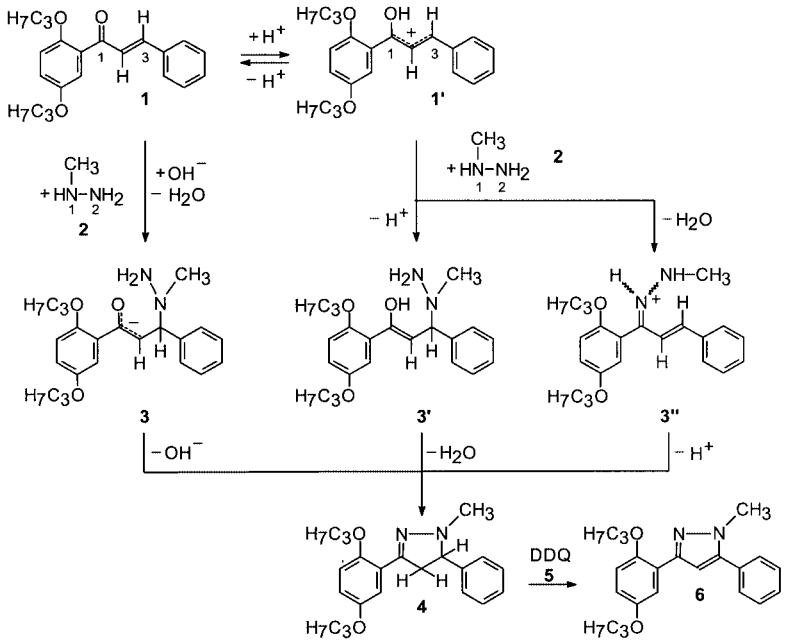


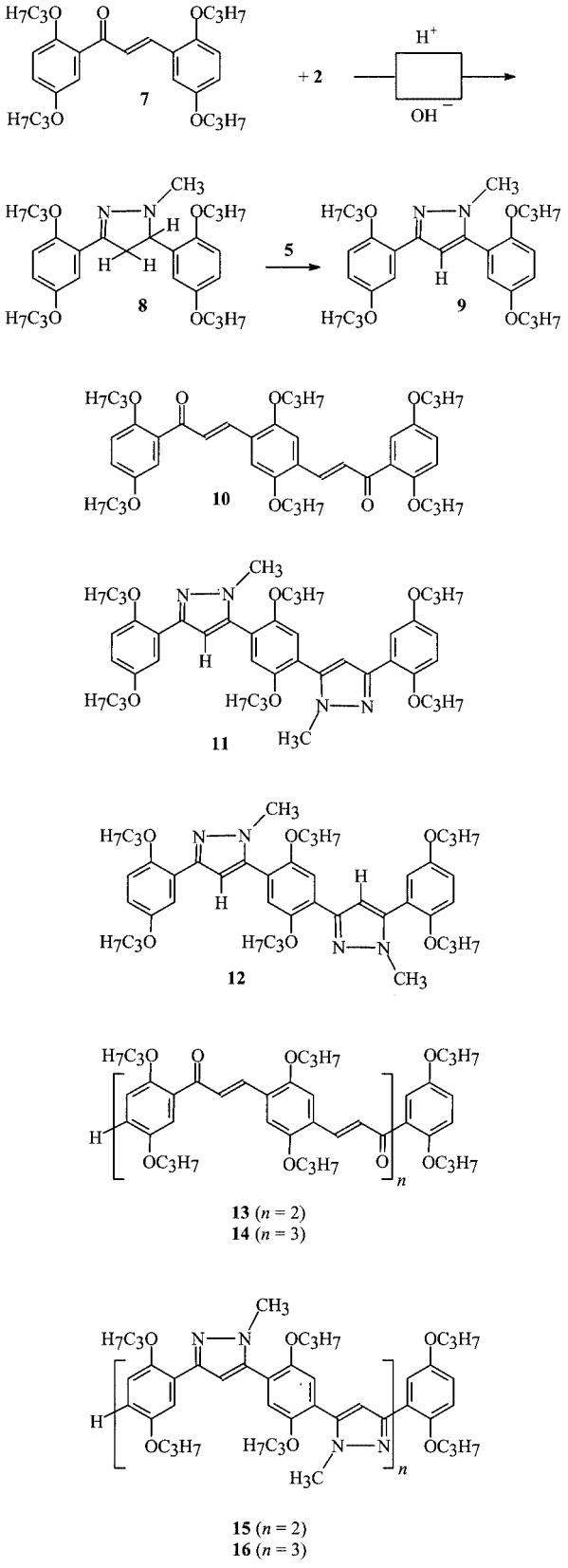
Scheme 2. Reaction of the unsymmetric chalcone **1** with methylhydrazine (**2**) and subsequent oxidation to the 1*H*-pyrazole **6**

Table 1. ^{1}H NMR spectroscopic data of the compounds **9**, **11**, **12** and **15**, δ values in $CDCl_3/C_6D_6$ (1:1), TMS as internal standard (the numbering corresponds to the nomenclature)

Compd.	3,5-Pyrazolylene		1,4-Phenylene	Phenyl[a]			Propoxy		
	1-CH_3 (s)	4-H (s)	3-H (s) 6-H (s)	3-H (d)	4-H (dd)	6-H (d)	OCH_2 (t)	CH_2 (m)	CH_3 (t)
9	3.63	6.96		6.67	6.72	7.81	3.54	1.43	0.70
				6.64	6.76	6.82	3.62	1.60	0.85
							3.67	1.60	0.83
							3.75	1.62	0.85
11	3.69	7.05	6.84	6.68	6.75	7.87	3.57	1.41−	0.71
							3.71	1.50	0.85
							3.77	(4 H)	0.87
								1.58−	
								1.67	
								(8 H)	
12	3.72	7.04	6.86	6.69	6.78	7.86	3.60	1.45−	0.73
	3.73	7.06	7.91	6.71	6.81	6.87	3.67	1.53	0.75
							3.73	(4 H)	0.75
							3.78	1.60−	0.89
							3.80	1.70	0.89
							3.80	(8 H)	0.90
15	3.74	7.06	6.89	6.74	6.78	7.86	3.62	1.50	0.90
	3.76	7.15	6.91				3.62	1.50	0.90
			7.96				3.74	1.66	0.89
							3.80	1.66	0.77
							3.98	1.71	0.75

[a] The upper δ values in this column belong to the phenyl group on C-3, the lower δ values to the phenyl group on C-5 of the pyrazole ring.

from the structure which was obtained for the reaction products of monosubstituted hydrazines and 1,4-bis(2-benzoylethenyl)benzene.[11] The propoxy groups in the enones were originally introduced to enhance the solubility and for the reduction of the HOMO−LUMO gap;[2,3] they may have weak steric and/or electronic effects, but they cannot change the reactivity towards hydrazines, as examples **1** and **7** demonstrate. We assume that the first regularly formed pyrazoline ring changes the regioselectivity for the formation of the second pyrazoline ring. Alkaline catalysis of the reaction **10** + **2** yielded pure **11**. Therefore, we subjected the higher oligomers **13** and **14** only to the alkaline variant. Oligochalcone **13** with four enone substructures furnishes **15** with four 1*H*-pyrazole units; however, the yield decreases to 12%, so it was not unexpected that oligochalcone **14**, with six enone units, gave only very small amounts



Scheme 3. Transformation of chalcones **7**, **10**, **13** and **14** to the 1*H*-pyrazoles **9**, **11**, **12**, **15** and **16**

of **16**, which represents a chain of 13 rings in an alternate sequence of benzene rings and 1*H*-pyrazole rings.

Structure elucidation of 2-pyrazolines **4** and **8** and 1*H*-pyrazoles **6**, **9**, **11**, **12** and **15** is mainly based on ^{1}H and ^{13}C NMR measurements including two-dimensional techniques such as TOCSY, ROESY, COSY, HMQC and HMBC.[21] The ^{1}H NMR spectra of **4** and **8** are characterized by AMX spin patterns for the protons on the 2-pyrazoline ring. The geminal coupling constant ^2J (4-H, 4-H) amounts to (−16.7 ± 0.1) Hz, the vicinal *trans* coupling constant $^3J_{trans}$ (4-H, 5-H) to (14.7 ± 0.2) Hz and the vicinal *cis* coupling constant $^3J_{cis}$ (4-H, 5-H) to 9.8 Hz. The chemical shift values are listed in the Exp. Sect.; the data prove unambiguously that the dipropoxyphenyl group in the unsymmetrical compound **4** is attached to C-3 of the 2-pyrazoline ring. The ^{1}H and ^{13}C NMR spectroscopic data of the 1*H*-pyrazoles **6**, **9**, **11**, **12** and **15** are summarized in Tables 1 and 2. In order to demonstrate the possibilities given by the two-dimensional measurements mentioned above, the complete correlation of the ^{1}H and ^{13}C NMR signals with certain nuclei of compound **9** is given in Figure 1; not only the two different benzene rings but even the four slightly different propoxy groups could be clearly discriminated.

Table 1. ^{13}C NMR spectroscopic data of the compounds **9**, **11**, **12** and **15**, δ values in $CDCl_3/C_6D_6$ (1:1), TMS as internal standard

Compd.	Pyrazole rings				Benzene rings			Propoxy groups		
	1-CH_3	C-3	HC-4	C-5	CH	C_q	C_qO	OCH_2	CH_2	CH_3
9	37.5	147.4	108.6	141.2	113.8	122.0	150.9	70.2	22.9	10.7
					114.5	124.0	151.0	70.2	22.9	10.7
					114.8		153.5	71.0	23.1	10.8
					115.4		153.8	71.3	23.1	11.0
					116.4					
					117.7					
11	37.4	147.2	108.4	140.5	113.5	122.0	150.4	69.8	22.5	10.3
					114.1	123.3	150.6	70.5	22.7	10.4
					115.2		153.5	70.8	22.8	10.6
					116.4					
12	37.6	146.9	108.6	141.2	113.2	120.3	150.6	70.2	23.0	10.6
					113.8	121.8	150.9	70.2	23.0	10.6
	37.7	147.4	108.8	141.4	114.5	123.8	151.0	70.2	23.1	10.8
					114.7	124.2	151.1	71.1	23.1	10.8
					115.1		153.5	71.2	23.1	11.0
					116.4		153.8	71.2	23.1	11.0
					116.5					
					117.8					
15	37.8	147.6	109.1	140.9	112.7	122.3	150.7	70.5	23.2	11.0
	37.8	147.6	109.4	141.1	113.8	122.3	150.7	71.3	23.2	11.0
					114.4	123.7	150.9	71.3	23.4	11.1
					115.5	123.7	151.1	71.5	23.5	11.3
					116.4		153.8	71.5	23.5	11.4
					116.8					

The UV spectra of the series **9**, **11** and **15** with one, two and four 1*H*-pyrazole rings, which are linked by 1,4-phenylene units, are shown in Figure 2. There is a small bathochromic shift (dotted line) of the long-wavelength absorption in the cross-conjugated oligomer series. A comparable result was found for the oligochalcone series **7**, **10** and **13**.[4] The conjugation in compounds **9**, **11** and **15** is additionally diminished by the torsion of the ring planes. The convergence of the λ_{max} values to a limiting value λ_∞ for increasing length of the cross-conjugated array of ring systems seems

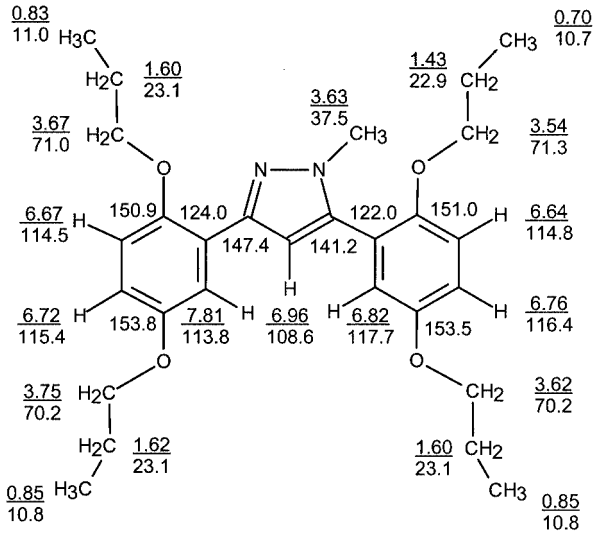


Figure 1. Correlation of the ^1H chemical shifts (upper values) and the ^{13}C chemical shifts (lower values) of **9** with certain protons and carbon atoms, respectively [measurement in $C_6D_6/CDCl_3$ (1:1), TMS as internal standard]

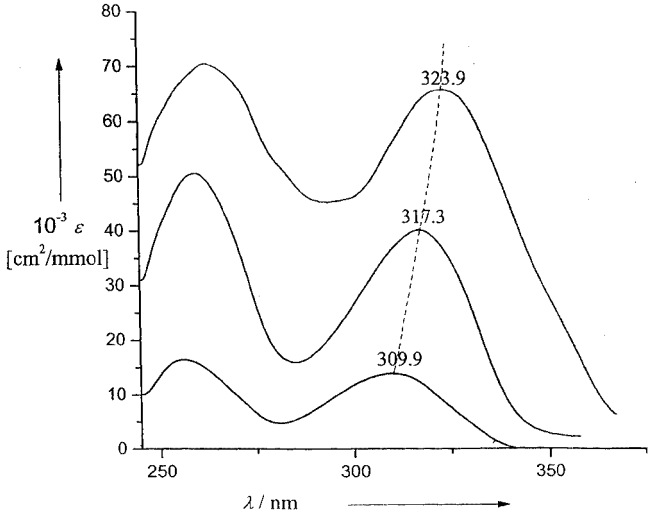


Figure 2. UV spectra of **9**, **11** and **15** (from bottom to top) measured in chloroform and the bathochromic shift of the long-wavelength absorption

to be slow; however, we did not attempt the calculation of λ_∞ and the effective conjugation length n_{ECL},[4] because the accuracy of the available spectrometer was ±1 nm and the increase of the λ_{max} values in the series **9**, **11**, **15** is relatively small (14 nm).

Conclusion

Cross-conjugated oligomers of alternating benzene and 1*H*-pyrazole rings can be obtained by reaction of the corresponding chalcones with methylhydrazine and subsequent oxidation with DDQ. Since monosubstituted hydrazines are bifunctional nucleophiles and enones are bifunctional electrophiles, four different primary steps are possible; nevertheless, a regioselective cyclization reaction is feasible by alkaline catalysis. The target compounds were characterized by their ^1H NMR, ^{13}C NMR, mass and UV spectra. Cross-conjugation in the "chain of rings" leads to a slight bathochromic shift of the long-wavelength absorption with increasing number of (hetero)aromatic rings.

Experimental Section

General: Melting points were determined with an SMP/3 apparatus from Stuart Scientifique and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded with Bruker AC-200, AC-300, AMX-400 and Avance 600 spectrometers; in order to obtain spectra without many superimposed signals, a 1:1 mixture of $CDCl_3$ and C_6D_6 was used as solvent, with TMS as internal standard. Mass spectra were obtained with a Finnigan MAT-95 instrument with the field desorption technique (FD) or with a Varian MAT-CH7A instrument with the electron impact method (EI, 70 eV). UV/Vis spectra were measured with a Zeiss MCS-320/340 spectrometer. Combustion analyses were performed with the Elementar Vario EL3 apparatus in the Chemistry Department of the University of Mainz.

Starting Compounds

(*E*)-1-(2,5-Dipropoxyphenyl)-3-phenyl-2-propen-1-one (1): A solution of 2,5-dipropoxyacetophenone[2] (1.0 g, 4.2 mmol) and benzaldehyde (0.56 mL, 0.588 g, 5.5 mmol) in ethanol (6 mL) was treated for 5 h with 1.5 M KOH (2.0 mL). Stirring was continued at ambient temperature for 30 h. Column chromatography (44 × 3 cm SiO_2, toluene/ethyl acetate, 40:1) yielded 820 mg (60%) of **1** as an almost colorless oil. ^1H NMR ($CDCl_3/C_6D_6$, 1:1): δ = 0.80 (t, 3 H, CH_3), 0.88 (t, 3 H, CH_3), 1.55 (m, 2 H, CH_2), 1.62 (m, 2 H, CH_2), 3.64 (t, 2 H, OCH_2), 3.68 (t, 2 H, OCH_2), 6.63 (d, 1 H, aromat. H, dipropoxyphenyl), 6.89 (dd, 1 H, aromat. H, dipropoxyphenyl), 7.13 (m, 3 H, aromat. H, phenyl), 7.28 (d, 1 H, aromat. H, dipropoxyphenyl), 7.38 (m, 2 H, aromat. H, phenyl), 7.48 (d, ^3J = 15.6 Hz, 1 H, 2-H), 7.68 (^3J = 15.6 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3/C_6D_6$, 1:1): δ = 10.3, 10.4 (CH_3), 22.5, 22.6 (CH_2), 69.9, 70.8 (OCH_2), 114.3, 115.0, 120.0 (aromat. CH, dipropoxyphenyl), 127.2, 135.3 (aromat. C_q), 128.3, 128.9 (aromat. CH, phenyl, partly superimposed), 129.9 (C-2), 142.2 (C-3), 152.1, 153.2 (aromat. C_qO), 191.8 (C-1) ppm. FD MS: *m*/*z* (%) = 324 (100) [M^+]. $C_{21}H_{24}O_3$ (324.4): calcd. C 77.75, H 7.46; found C 77.78, H 7.28.

The enones **7**, **10**, **13** and **14** were prepared according to literature methods.[2,3]

Preparation of 1*H*-Pyrazoles 6 and 9 via 2-Pyrazolines 4 and 8 in the Protic Solvent Methanol: Methylhydrazine (**2**) (0.22 mL, 0.19 g, 4.13 mmol) in methanol (1.0 mL) was slowly added dropwise at 0 °C under argon to a solution of enone **1** (0.325 g, 1.0 mmol) in dry methanol (20 mL). After about 15 min of stirring, **4** started to precipitate from the light-yellow solution. TLC (SiO_2, toluene/ethyl acetate, 15:1) showed that the reaction had ended after about 1 h. The precipitate of **4** was washed with *n*-hexane (10 mL) and recrystallized from ethanol (yield 202 mg, 57%, m.p. 89 °C).

The analogous reaction of enone **7** and **2** is somewhat slower, so the mixture was refluxed for 45 min. Column chromatography (35 × 1.5 cm SiO_2, toluene/ethyl acetate, 10:1) of the residue yielded 66% of **8**, an oil which already contained some autoxidation product **9**. The regular oxidation of **4** and **8** was achieved in situ with DDQ (**5**) (96 mg, 0.42 mmol) in boiling benzene (3.0 mL). After 1 h, the raw products were purified by column chromatography (35

× 1.5 cm SiO_2, toluene/ethyl acetate, 15:1); **6** could be obtained from **1** in a yield of 74% and **9** in a yield of 78% (from **7**).

***rac*-3-(2,5-Dipropoxyphenyl)-1-methyl-5-phenyl-4,5-dihydro-1*H*-pyrazole (4) and 3-(2,5-Dipropoxyphenyl)-1-methyl-5-phenyl-1*H*-pyrazole (6):** The intermediate 2-pyrazoline ***rac*-4** was characterized by NMR spectroscopy and mass spectrometry; the raw product is sufficiently pure for the subsequent oxidation with DDQ (**5**). **4**: ^{1}H NMR ($CDCl_3/C_6D_6$, 1:1): δ = 0.79 (t, 3 H, CH_3), 0.88 (t, 3 H, CH_3), 1.50 (m, 2 H, CH_2), 1.63 (m, 2 H, CH_2), 2.74 (s, 3 H, NCH_3), 3.07 (dd, ^2J = −16.8, ^3J = 14.9 Hz, 1 H, 4-H), 3.57 (m, 2 H, OCH_2), 3.61 (dd, ^2J = −16.8, ^3J = 9.8 Hz, 1 H, 4-H), 3.72 (t, 3 H, OCH_2), 3.91 (dd, ^3J = 14.9, ^3J = 9.8 Hz, 1 H, 5-H), 6.58 (d, ^3J = 9.0 Hz, 1 H, 3-H, dipropoxyphenyl), 6.76 (dd, ^3J = 9.0, ^4J = 3.1 Hz, 4-H, dipropoxyphenyl), 7.12 (m, 1 H, 4-H, phenyl), 7.20 (m, 2 H, 3-H, 5-H, phenyl), 7.38 (m, 2 H, 2-H, 6-H, phenyl), 7.57 (d, ^4J = 3.1 Hz, 1 H, 6-H, dipropoxyphenyl) ppm. ^{13}C NMR ($CDCl_3/C_6D_6$, 1:1): δ = 10.7, 10.8 (CH_3), 22.9, 23.0 (CH_2), 41.8 (NCH_3), 46.9 (C-4), 70.1, 70.7 (OCH_2), 74.6 (C-5), 113.8, 114.1, 117.1 (C-3, C-4, C-6, dipropoxyphenyl), 123.4 (C-1, dipropoxyphenyl), 127.8, 128.8, 128.8 (C-2, C-3, C-4, C-5, C-6, phenyl), 141.2 (C-1, phenyl), 149.7 (C-3), 151.5, 153.5 (C-2, C-5, dipropoxyphenyl) ppm. EI MS (70 eV): *m*/*z* (%) = 352 (100) [M$^+$], 309 (24), 275 (14). On standing in solution, the compound shows a dehydrogenation to pyrazole **6**, which is formed by oxidation of the raw product **4** with DDQ (**5**); see above. Pyrazole **6** is a colorless solid which melts at 75 °C. ^{1}H NMR ($CDCl_3/C_6D_6$, 1:1): δ = 0.90 (t, 3 H, CH_3), 0.91 (t, 3 H, CH_3), 1.66 (m, 4 H, CH_2), 3.64 (s, 3 H, NCH_3), 3.72 (t, 2 H, OCH_2), 3.80 (t, 2 H, OCH_2), 6.70 (d, ^3J = 9.3 Hz, 1 H, 3-H, dipropoxyphenyl), 6.77 (dd, ^3J = 9.3, ^4J = 2.6 Hz, 1 H, 4-H, dipropoxyphenyl), 7.01 (s, 1 H, 4-H), 7.18 (m, 3 H, *m*-H, *p*-H, phenyl), 7.28 (m, 2 H, *o*-H, phenyl), 7.81 (d, ^4J = 2.6 Hz, 1 H, 6-H, dipropoxyphenyl) ppm. ^{13}C NMR ($CDCl_3/C_6D_6$, 1:1): δ = 10.4, 10.6 (CH_3), 22.7, 22.8 (CH_2), 37.1 (NCH_3), 69.9, 70.6 (OCH_2), 107.6 (C-4), 113.7, 114.1, 115.2 (aromat. CH, dipropoxyphenyl), 123.4, 150.6, 153.5 (aromat. C_q, dipropoxyphenyl), 128.0, 128.5, 128.6 (aromat. CH, phenyl), 131.2 (aromat. C_q, phenyl), 143.8 (C-5), 147.4 (C-3) ppm. FD MS: *m*/*z* (%) = 351 (100) [M + H$^+$]. $C_{22}H_{26}N_2O_2$ (350.48): calcd. C 75.40, H 7.48, N 7.99; found C 75.39, H 7.51, N 7.99.

3,5-Bis(2,5-dipropoxyphenyl)-1-methyl-4,5-dihydro-1*H*-pyrazole (8) and 3,5-Bis(2,5-dipropoxyphenyl)-1-methyl-1*H*-pyrazole (9): The intermediate 2-pyrazoline **8** was obtained in a yield of 66%; it is a colorless oil. The compound, which is not stable in air, was characterized by its ^{1}H NMR, ^{13}C NMR and mass spectra. ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, 3 H, CH_3), 1.00 (t, 6 H, CH_3), 1.02 (t, 3 H, CH_3), 1.67−1.82 (m, 8 H, CH_2), 2.81 (dd, ^2J = −16.6, ^3J = 14.6 Hz, 1 H, 4-H), 2.83 (s, 3 H, NCH_3), 3.75−3.93 (m, 9 H, OCH_2 and 4-H), 4.44 (dd, ^3J = 14.6, ^3J = 9.8 Hz, 1 H, 5-H), 6.70−6.85 (m, 4 H, aromat. H), 7.23 (m, 1 H, aromat. H), 7.35 (m, 1 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.5, 10.5, 10.8, 10.8 (CH_3), 22.7, 22.7, 22.7, 22.8 (CH_2), 42.2 (NCH_3), 44.7 (C-4), 67.5 (C-5), 70.2, 70.2, 70.3, 70.8 (OCH_2), 112.5, 113.4, 113.8, 113.8, 113.9, 116.9 (aromat. CH), 130.6 (aromat. C_q), 149.1 (C-3), 151.1, 151.4, 153.1, 153.4 (aromat. C_qO) ppm. FD MS: *m*/*z* (%) = 468 (100) [M$^+$]. On standing in solution, **8** shows a slow dehydrogenation to pyrazole **9**, which is formed by oxidation of the raw product **8** with DDQ (**5**). Pyrazole **9** is a yellowish oil.[22] UV ($CHCl_3$): λ_{max} = 256 nm (ε = 16420 cm^2·mmol^{-1}), 310 nm (ε = 13850 cm^2·mmol^{-1}). FD MS: *m*/*z* (%) = 467 (100) [M$^+$]. $C_{28}H_{38}N_2O_4$ (466.6): calcd. C 72.07, H 8.21, N 6.00; found C 72.11, H 8.11, N 6.00.

The analogous reaction of **10** and **2** and the subsequent oxidation with **5** led to a mixture of the bis(pyrazols) **11** and **12**, which could not be separated. According to the ^{1}H NMR spectrum of the mixture the ratio **11**:**12** amounts to 44:56.

Preparation of 1*H*-Pyrazoles 6, 9, 11 and 15 in the Presence of Alkali: Methylhydrazine (**2**) (4.0 mmol, 0.185 g per enone unit) was slowly added to **1**, **7**, **10** or **13** (1.0 mmol) and KOH (1.5 g, 27 mmol) in ethanol (150 mL), under argon at room temperature. After refluxing for 1.5 h, the reaction mixture was filtered and concentrated to dryness. The residue was dissolved in chloroform (80 mL), washed with water (40 mL) and dried with Na_2SO_4. The crude pyrazolines were oxidized in benzene (15 mL) with DDQ (**5**) (0.3 g, 1.3 equiv. per pyrazoline ring). After refluxing for 1 h, the mixture was filtered and the residue washed with toluene (10 mL). The concentrated filtrate was subjected to column chromatography (3 × 44 cm SiO_2, toluene/ethyl acetate, 5:1). The target compounds **6**, **9**, **11** and **15** could be obtained in yields of 68, 78, 38 and 12%, respectively.

5,5-(2,5-Dipropoxy-1,4-phenylene)bis[3-(2,5-dipropoxyphenyl)-1-methyl-1*H*-pyrazole] (11): Yield 38%, almost colorless solid, m.p. 153 °C.[22] UV ($CHCl_3$): λ_{max} = 259 nm (ε = 50520 cm^2·mmol^{-1}), 317 nm (ε = 40220 cm^2·mmol^{-1}). FD MS: *m*/*z* (%) = 739 (100) [M$^+$]. $C_{44}H_{58}N_4O_6$ (738.9): calcd. C 71.52, H 7.91, N 7.58; found C 71.53, H 8.02, N 7.41.

3-(2,5-Dipropoxyphenyl)-5-{4-[5-(2,5-dipropoxyphenyl)-1-methyl-1*H*-pyrazol-3-yl]2,5-dipropoxyphenyl}-1-methyl-1*H*-pyrazole (12): As discussed above, the reaction mixture **11**/**12** could not be separated. Since **11** could be selectively formed by applying base catalysis, the ^{1}H and ^{13}C NMR signals of **12**, listed in Tables 1 and 2, were obtained from the spectra of the mixture.

3,3′-(2,5-Dipropoxy-1,4-phenylene)bis(5-{4-[3-(2,5-dipropoxyphenyl)-1-methyl-1*H*-pyrazol-5-yl]-2,5-dipropoxyphenyl}-1-methyl-1*H*-pyrazole) (15): Yield 12%, m.p. 192 °C.[22] UV ($CHCl_3$): λ_{max} = 262 nm (ε = 70460 cm^2·mmol^{-1}), 324 nm (ε = 65830 cm^2·mmol^{-1}). FD MS: *m*/*z* (%) = 1282 (100 [M$^+$]. $C_{76}H_{98}N_8O_{10}$ (1282.7): calcd. C 71.11, H 7.70, N 8.73; found C 71.08, H 7.68, N 8.75.

5,5′-(2,5-Dipropoxy-1,4-phenylene)bis{3-[4-(5-{4-[3-(2,5-dipropoxylphenyl)-1-methyl-1*H*-pyrazol-5-yl]-2,5-dipropoxyphenyl}-1-methyl-1*H*-pyrazol-3-yl)-2,5-dipropoxy-phenyl]-1-methyl-1*H*-pyrazole} (16): The yield of the compound is so low that we did not attempt an isolation and purification. The FD MS spectrum showed unambiguously the expected molecular ions at *m*/*z* (%) = 1228 (100).

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[22] The ^{1}H and ^{13}C NMR spectroscopic data are summarized in Tables 1 and 2. TMS as internal standard; the numbering corresponds to the nomenclature.

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