Electronic supplementary materials *Mendeleev Commun.*, 2014, **24**, 377−379

Synthesis and conformations of cross-conjugated polyenes containing heterocyclic moieties with diverse structures

Zhanna A. Krasnaya, Vadim V. Kachala and Sergei G. Zlotin

Experimental

The ^{1}H and ^{13}C NMR spectra of compounds **12a-e**, **13a-e** and **14** were recorded on a Bruker Avance II 600 instrument equipped with an inverse probe with Z-gradient, in DMSO-d_6 or in $CDCl_3$. The ^{13}C and ^{1}H chemical shifts were calibrated using the signals of carbon atoms (δ 39.50) and residual protons (δ 2.50) of DMSO. Two-dimensional experiments were carried out by the standard Bruker procedures using Z-gradient pulses. The mixing time in the NOESY spectrum was 0.7 s. HMBC experiments were optimised for a ^{1}H-^{13}C coupling constant of 10 Hz. High resolution mass spectra were recorded on a Bruker micrOTOF instrument by using the electrospray ionization method (ESI). High resolution mass spectra were measured at Department of structural measurements of the N.D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Moscow. Electronic absorption spectra were recorded using a Specord UV-VIS spectrophotometer. The reactions were monitored by UV spectroscopy.

Synthesis of starting compounds

4-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (10a).[1] ^{1}H NMR ($CDCl_3$, δ): 2.30 (s, 3H, 2-Me); 2.35 (s, 3H, 6-Me); 2.45 (s, 3H, 8-Me); 6.70 (s, 1H, H-5); 7.10 (t, 1H, Ph); 7.45 (t, 2H, Ph); 8.00 (d, 2H, Ph); 8.5 (s, 1H, H-3).

3-Methyl-1-phenyl-4-(1,2,6-trimethylpyridin-4(1*H*)-ylidene)-1*H*-pyrazol-5(4*H*)-one (11a).[1] ^{1}H NMR (DMSO-d_6, δ): 2.35 (s, 3H, 2-Me); 2.50 (s, 3H, 6-Me); 3.51 (s, 3H, 1-Me); 2.45 (s, 3H, 8-Me); 7.0 (t, 1H, Ph); 7.90 (br.s, 2H, H-3, H-5); 7.30 (t, 2H, Ph); 8.10 (d, 2H, Ph).

4-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-3-phenylisoxazol-5(4*H*)-one (10b).[2] ^{1}H NMR ($CDCl_3$, δ): 2.10 (s, 3H, Me); 2.38 (s, 3H, Me); 6.10 (s, 1H, H-5); 7.51 (m, 5H, Ph); 8.21 (s, 1H, H-3).

3-Phenyl-4-(1,2,6-trimethylpyridin-4-(1*H*)-ylidene)isoxazol-5(4*H*)-one (11b). A reaction mixture containing 4-(2,6-dimethyl-4*H*-pyran-4-ylidene)-3-phenyloxazol-5(4*H*)-one **10b** (0.3 g, 1.12 mmol), 15% $MeNH_2$ solution in EtOH (2 ml) and EtOH (15 ml) was stirred for 5 h under reflux conditions. Next day, the flaky precipitate was isolated and washed with dry EtOH to give 0.2 g (65%) of substituted dihydropyridine **11b** as needle-like lemon-coloured crystals, mp 250-252°C. UV, λ_{max}/nm: 375 (EtOH). Mass spectrum (ESI), *m/z* $[M+H]^+$ found: 281.1282, calculated 281.1285, $C_{17}H_{16}N_2O_2$. (DMSO-d_6, δ): 2.33 (s, 6H, 2-Me, 6-Me); 3.65 (s, 3H, 1-Me); 7.20-7.50 (m, 7H, H-3, H-5, Ph).

4-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-1,2-diphenylpyrazolidine-3,5-dione (10c). A mixture of 1,2-diphenylpyrazolidine-3,5-dione (2.52 g, 10 mmol), 2,6-dimethylpyrone (1.24 g, 10 mmol) and acetic anhydride (30 ml) was stirred for 5 h under reflux conditions. The mixture was cooled and a precipitate was isolated, washed three times with a $NaHCO_3$ solution, then washed with EtOH and dry ether to give 2.6 g of diketone **10c**, which was stirred for 30 min with 20 ml of dry EtOH under reflux conditions. After cooling, 2.27 g (63%) of diketone **10c** was separated, sandy crystals, mp >250°C. UV, λ_{max}/nm 375 split (EtOH), 375 split ($CHCl_3$). Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 359.1385, calculated 359.1390, $C_{22}H_{18}N_2O_3$. (DMSO-d_6, δ): 2.45 (s, 6H, Me); 7.1 (m, 2H, Ph); 7.32 (m, 8H, Ph); 8.15 (s, 2H, H-3, H-5); ($CDCl_3$, δ): 2.40 (s, 6H, Me); 7.1 (m, 2H, p-Ph); 7.32 (m, 4H, m-Ph); 7.45(m, 4H, o-Ph); 8.23 (s, 2H, H-3, H-5).

1,2-Diphenyl-4-(1,2,6-trimethylpyridin-4(1*H*)-ylidene)pyrazolidine-3,5-dione (11c). A mixture of diketone **10c** (0.5 g, 1.4 mmol), 40% aqueous $MeNH_2$ (3 ml) and EtOH (90 ml) was stirred for 3 h under reflux conditions. After 24 h a precipitate was separated, washed with EtOH and acetone to give 0.45 g (86%) of diketone **11c** as colorless crystals, mp >250°C. UV, λ_{max}/nm: 365 (EtOH), 380 ($CHCl_3$). Mass spectrum (ESI), *m/z*: $[M+H]^+$, found 372.1699, calculated 372.1707, $C_{23}H_{21}N_3O_2$. (DMSO-d_6, δ): 2.55 (s 6H, Me), 3.71 (s, 3H, 1-Me); 7.02 (m, 2H, p-Ph), 7.26 (m, 4H, m-Ph), 7.35 (m, 4H, o-Ph); 8.36 (s, 2H, H-3, H-5).

5-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (10d). A mixture of 1.3-dimethylbarbituric acid (1.56 g, 10 mmol), 2,6-dimethylpyrone (1.24 g, 10 mmol) and acetic anhydride (20 ml) was stirred for 5 h under reflux conditions. Next day, a light yellow needle-like precipitate was isolated and repeatedly washed with a $NaHCO_3$ solution

and then with hot EtOH. Drying *in vacuo* gave 2.5 g (95%) of triketone **10d** as needle-like crystals, mp >245°C. UV, λ_{max}/nm: 390, sh 370 ($CHCl_3$). Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 263.1036, calculated 263.1026, $C_{13}H_{14}N_2O_4$. ($CDCl_3$, δ): 2.35 (s, 6H, Me); 3.30 (s, 6H, NMe); 8.85 (s, 2H, H-3, H-5).

1,3-Dimethyl-5-(1,2,6-trimethylpyridin-4(1*H*)-ylidine)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (11d). A mixture of triketone **10d** (0.5 g, 1.9 mmol), 40% aqueous $MeNH_2$ (3 ml) and EtOH (100 ml) was stirred for 3 h under reflux conditions. The reaction mixture was concentrated by 2/3 *in vacuo* and cooled. A precipitate was isolated, washed with EtOH and acetone. Drying *in vacuo* gave 0.47 g (89%) of triketone **11d** as colorless crystals, mp >250°C. UV, λ_{max}/nm: 380 ($CHCl_3$). Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 275.1273, calculated 275.1264, $C_{14}H_{17}N_3O_3$. (DMSO-d_6, δ): 2.55 (s, 6H, Me); 3.15 (s, 6H, NMe); 3.75 (s, 3H, 1-Me); 8.82 (s, 2H, H-3, H-5).

1,3-Diethyl-5-(2,6-dimethyl-4*H*-pyran-4-ylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (10e).[2] UV, λ_{max}/nm: 420 ($CHCl_3$), 415 (EtOH).

1,3-Diethyl-2-thioxo-5-(1,2,6-trimethylpyridin-4(1*H*)-ylidene)dihydropyrimidine-4,6(1*H*,5*H*)-dione (11e). A mixture of diketone **10e** (0.5 g, 1.6 mmol), 40% aqueous $MeNH_2$ (3 ml) and EtOH (100 ml) was stirred for 2 h under reflux conditions and then concentrated *in vacuo*. A 1:1 mixture of EtOH and acetone (30 ml) was added with stirring to the precipitate and the system was stirred for 30 min under reflux conditions. After cooling, a precipitate was separated and washed with an EtOH:acetone mixture to give 0.4 g (80%) of dihydropyrimidine **11e** as light yellow crystals, mp >250°C. UV, λ_{max}/nm: 405 ($CHCl_3$). Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 320.1434, calculated 320.1427, $C_{16}H_{21}N_3O_2S$. (DMSO-d_6, δ): 1.15 (t, 6H, $NCH_2C\underline{H}_3$); 2.60 (s, 6H, Me); 3.70 (s, 3H,1-Me); 4.45 (q., 4H, $NC\underline{H}_2CH_3$); 8.80 (s, 2H, H-3, H-5).

References

1. J. Kelemen and R. Wizinger, *Helv. Chim. Acta*, 1962, **45**, 1908.
2. G. Koeckelberghs, L. D. Groof, J. Perez-Moreno, JAsselberghs, K. Clays, Th. Verbiest and C. Samyn, *Tetrahedron*, 2008, **64**, 3772.

4-[2,6-Bis((1*E*,3*E*)-4-dimethylaminobuta-1,3-dienyl)-4*H*-pyran-4-ylidene]-1,2-diphenyl-pyrazolidine-3,5-dione (12c). A mixture of substituted pyran **10c** (0.15 g, 0.42 mmol) and

aminal **1** (0.22 g, 1.28 mmol) was stirred for 20 min at 20°C and then for 15 min at 55-60°C to give a very dark precipitate. The reaction mixture was concentrated *in vacuo*. Dry Et_2O was added to the crystalline precipitate; the precipitate was filtered off and washed with dry MeOH for 20 min with stirring. The precipitate was filtered off and washed with dry Et_2O to give 0.18 g (54%) of polyene **12c** as black crystals, mp >240°C. Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 521.2541, calculated 521.2547 $C_{32}H_{32}N_4O_3$. UV, λ_{max}/nm (ε): 380, 490, 580 (EtOH); 360 (32933), 390 (27733), 490 (69334), 555 (39867) ($CHCl_3$). ^{1}H NMR ($CDCl_3$, δ): 5.81 (d, 2H, H-α, J 14.4); 7.18 (dd, 2H, H-β, J 14.4, J 12.1); 5.21 (t, 2H, H-γ, J 12.1); 6.70 (d, 2H, H-δ, J 12.1); 8.06 (s, 2H, H-3, H-5); 2.92 (s, 12H, NMe_2); 7.1-7.45 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, δ): 152.63 (C-2, C-6), 104.73 (C-3, C-5), 87.55 (C-4), 163.44 (C-7), 168.55 (C-8, C-11), 108.37 (C-α), 140.37 (C-β), 98.74 (C-γ), 150.14 (C-δ), 40.82 (NMe_2), 139.53, 125.39, 128.45, 122.13 (Ph).

2-[2,6-Bis((1*E*,3*E*)-4-dimethylaminobuta-1,3-dienyl)-1-methylpyridin-4-(1*H*)-ylidine]-*N'*-formyl-*N*,*N'*-diphenylpropanehydrazide (13c). A mixture of substituted dihydropyridine **11c** (0.2 g, 0.54 mmol) and aminal **1** (0.28 g, 1.6 mmol) was stirred for 1 h at 60-65°C and then concentrated *in vacuo*. Dry Et_2O was added to the residue. A precipitate was isolated and washed with dry Et_2O and EtOH. Dry MeOH (3 ml) was added to the precipitate and the mixture was stirred for 30 min at 40°C to give 0.18 g (64%) of polyene **13c** as light-brown crystals, mp 234-236°C. Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 534.2860, calculated 534.2864 $C_{33}H_{35}N_5O_2$. UV, λ_{max}/nm (ε): 425 (22868), 495 (41163), (EtOH); 270 (27600), 355 (18400), plateau 430 (47840), 475(60720) ($CHCl_3$). ^{1}H NMR (DMSO-d_6, δ): 6.11 (d, 2H, H-α, J 14.5); 7.05 (dd, 2H, H-β, J 11.0, J 14.5); 5.31 (t, 2H, H-γ, J 12.0); 7.02 (m, 2H, H-δ); 8.48 (s, 2H, H-3, H-5); 7.23-7.40 (m, 10H, Ph); 3.67 (s, 3H, NMe); 2.89 (s, 12H, NMe_2). ^{13}C NMR (DMSO-d_6, δ): 151.04 (C-2, C-6), 107.77 (C-3, C-5), 121.40 (Ph), 128.10 (Ph), 168.40 (C-8); 108.15 (C-α); 141.53 (C-β); 97.77 (C-γ); 150.46 (C-δ); 37.61 (NMe); 39.71 (NMe_2).

5-[2,6-Bis((1*E*,3*E*)-4-dimethylaminobuta-1,3-dienyl)-4*H*-pyran-4-ylidene]-1,3-dimethyl-pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (12d). A mixture of pyrimidinetrione **10d** (0.1 g, 0.4 mmol) and aminal **1** (0.2 g, 1.17 mmol) was stirred for 3.5 h at 20°C. The heterogeneous reaction mixture was concentrated *in vacuo*. The residue was repeatedly washed with dry Et_2O, and then 2 ml of EtOH was added. In 1 h, a dark-violet crystalline precipitate was isolated. The yield of polyene **12d** was 0.14 g (87%), mp 223-225°C. Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 425.2185, calculated 425.2169 $C_{23}H_{28}N_4O_4$. UV, λ_{max}/nm (ε): 365 (28845), 400 (35208), 500 (57267), 615 (30542) (EtOH); 360 (48359), 390 (37330), 495 (82295), 575 (47510) ($CHCl_3$). ^{1}H NMR (DMSO-d_6, δ): 5.80 (d, 2H, H-α, J 14.6); 7.36 (dd, 2H, H-β, J 14.2, J 12.1); 5.34 (t, 2H, H-

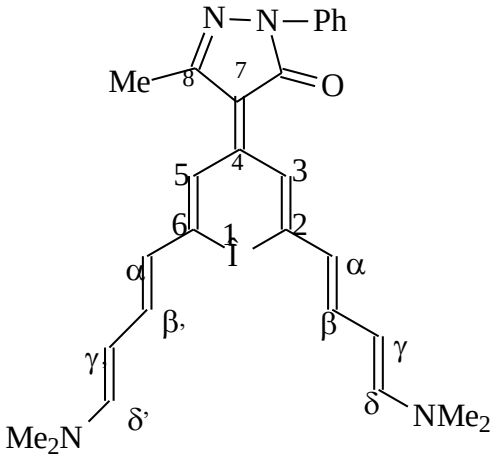
γ, J 12.0); 7.21 (d, 2H, H-δ, J 12.4); 3.15 (s, 6H, CONMe); 2.95 (s, 12H, NMe_2); 8.20 (s, 2H, H-3, H-5).

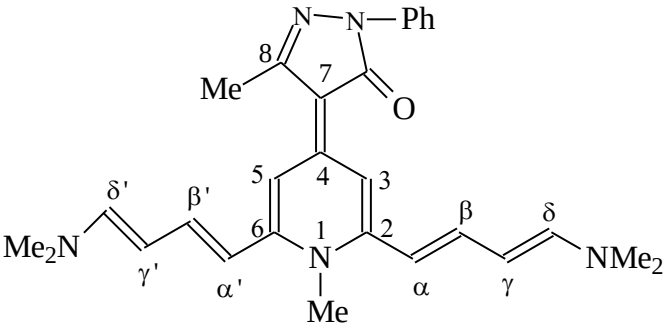
5-[2,6-Bis((1*E*,3*E)*-4-dimethylaminobuta-1,3-dienyl)-1-methylpyridin-4(1*H*)-ylidene]-1,3-dimethylpyridimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**13d).** A mixture of pyrimidinetrione **11d** (0.2 g, 0.7 mmol) and aminal **1** (0.4 g, 2.1 mmol) was stirred for 1 h 40 min at 70°C to give a dense orange precipitate. The reaction mixture was concentrated *in vacuo*. Dry Et_2O was added to the residue and the precipitate was filtered off. EtOH (5 ml) was added to the solid and the mixture was boiled for 10 min and then cooled. The crystalline precipitate was separated and washed with dry ether. The yield of polyene **13d** was 0.25 g (80%), orange crystals, mp >240°C. Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 438.2489, calculated 438.2500 $C_{24}H_{31}N_5O_3$. UV, λmax/nm (ε): 355 (20169), 415 (24202), 495 (47069) (EtOH), 355 (18824), 430 sh (32364), 480 (55801) ($CHCl_3$). ^{1}H NMR (DMSO-d_6, δ): 6.11 (d, 2H, H-α, J 14.6); 7.01 (dd, 2H, H-β, J 12.0, J 14.5); 5.28 (t, 2H, H-γ, J 11.9); 7.09 (d, 2H, H-δ, J 11.9); 3.67 (s, 3H, NMe); 3.17 (s, 6H, CONMe); 2.90 (s, 12H, NMe_2); 8.79 (s, 2H, H-3, H-5). ^{13}C NMR (DMSO-d_6, δ): 110 (C-α), 142.13 (C-β), 98.23 (C-γ), 150.15 (C-δ), 40.14 (NMe_2), 39.23 (NMe), 29.05 (CONMe), 113.06 (C-3, C-5).

5-[2,6-Bis(1*E*,3*E*)-4-dimethylaminobuta-1,3-dienyl)-4*H*-pyran-4-ylidene]-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (12e). Aminal **1** (0.33 g, 1.95 mmol) was added with stirring to dihydropyrimidinedione **10e** (0.2 g, 0.65 mmol). After 30 min, dry benzene (1.8 ml) was added. The mixture was kept for 2 h and concentrated *in vacuo* at 40°C. The residue was repeatedly washed with dry ether, dissolved in a small amount of EtOH and poured into 30 ml of distilled water. After 15 min the precipitate was filtered off and washed with H_2O and Et_2O. Drying *in vacuo* gave 0.17 g (57%) of polyene **12e** as dark-brown crystals, mp 230-232°C. Mass spectrum (ESI), *m/z*: $[M+H]^+$ found 469.2268, calculated 469.2275 $C_{25}H_{32}N_4O_3S$. UV, λ_{max}/nm (ε): 365(11429), 410 (14286), 510 (27716), 625 (13715) (EtOH); 365 (44103), 400 (31240), 510 (83613), 590 (47779) ($CHCl_3$). ^{1}H NMR (DMSO-d_6, δ): 5.82 (d, 2H, H-α, J 14.5); 7.42 (dd, 2H, H-β, J 11.5, J 14.6); 5.39 (t, 2H, H-γ, J 12.0); 7.29 (d, 2H, H-δ, J 12.3); 2.97 (s, 12H, NMe_2); 8.09 (s, 2H, H-3, H-5); 1.17 (t, 6H, $NCH_2C\underline{H}_3$, J 6.8); 4.44 (q, 4H, $NC\underline{H}_2CH_3$, J 6.8). ^{13}C NMR (DMSO-d_6, δ) 106.96 (C-α); 142.69 (C-β); 98.70 (C-γ); 153.35 (C-δ); 39.64 (NMe_2); 107.36 (C-3, C-5); 12.45 ($NCH_2C\underline{H}_3$);42.04 ($NC\underline{H}_2CH_3$); 160.42 (C=O); 162.76 (C-2, C-6); 175.76 (C=S).

Table S1 Correlation data in ROESY experiments (DMSO-d_6, t=80°C) for polyene **12a.**

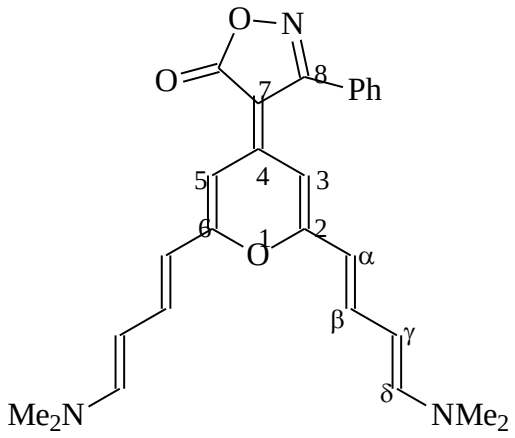
Table S2 ^{1}H-^{1}H and ^{1}H-^{13}C correlation data in NOESY and HMBC experiments, respectively (DMSO-d_6) for polyene **13a.**





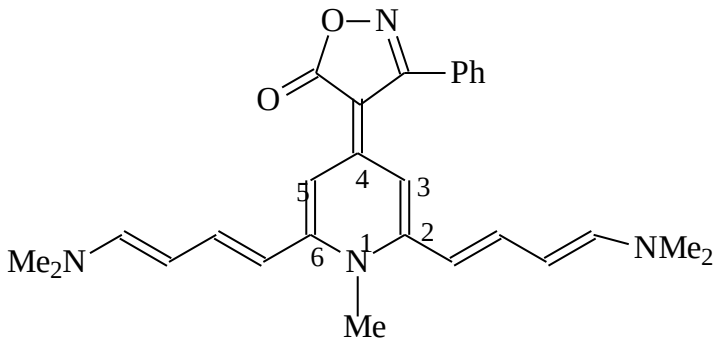
Атом	ROESY H	Атом	NOESY H	HMBC H/C
H(α)	H(γ), H(3)	N-Me	H(α)	C(2), C(6)
H(α’)	H(γ’), H(5)	C(3)H	H(β)	C(α), C(2)
H(β)	H(δ)	C(5)H	H(β’)	C(α’), C(6)
H(β’)	H(δ’)	H(α)	NMe,H(γ)	C(γ), C(3), C(β)
H(γ)	H(α), NMe_2	H(α’)	N-Me,H(γ’)	C(γ’), C(5), C(β)
H(γ’)	H(α’), NMe_2	H(β)	H(3), H(δ)	C(γ) (Cδ)
H(δ)	NMe_2, (Hβ)	H(β’)	H(5), H(δ)	C(γ’) (Cδ·)
H(δ’)	NMe_2, (Hβ’)	H(γ)	H (α), NMe_2	C(α), C (β)
NMe_2	H(δ), H(γ)	H(γ’)	H (α’), NMe_2	C(α’), C (β’)
C(3)H	H(α)	H(δ)	H(β), NMe_2	C(γ), C(β), NMe_2
C(5)H	H(α,), 8-CH_3	H(δ’)	H(β’), NMe_2	C(γ’), C(β’), NMe_2
8-CH_3	H (5)	O-CHarom.	m-Ph	
		m-CHarom	p-Ph, o-Ph	
		p-CHarom	m-Ph	
		NMe_2	H(γ), H(δ)	C(δ)

Table S3 ^{1}H-^{1}H correlation data in ROESY experiments (DMSO-d_6, t=80°C) for polyene **12b.**



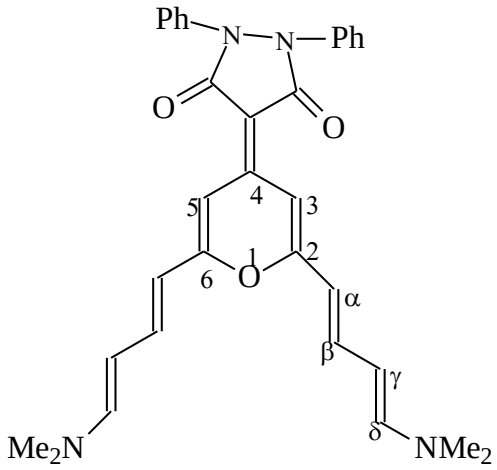
Atom	ROESY, H
H(α)	H(3),H(5),H(γ)
H(β)	H(δ)
H(γ)	NMe_2
H(δ)	NMe_2, H(β)
C(3)H, C(5)H	H(α)
NMe_2	H(γ),H(δ)

Table S4 ^{1}H-^{1}H correlation data in ROESY experiments (DMSO-d_6) for polyene **13b.**



Atom	NOESY, H
H(α)	NMe, H(γ)
H(β)	H(3),H(5), H(δ)
H(γ)	H(α), NMe_2
H(δ)	NMe_2, H(β)
C(3)H,C(5)H	H(β), H(δ)
NMe	H(α)
NMe_2	H(δ)

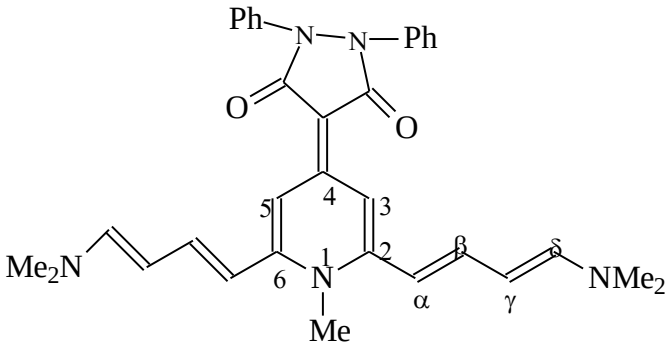
Table S5 ^{1}H-^{1}H correlation data in NOESY experiments ($CDCl_3$) for polyene **12c.**



Atom	NOESY, H
C(3)H, C(5)H	H(α)
H(α)	H(3), H(5), H(γ)
H(β)	H(δ)
H(γ)	H(α), NMe_2
H(δ)	H(β), NMe_2
NMe_2	H(γ), H(δ)

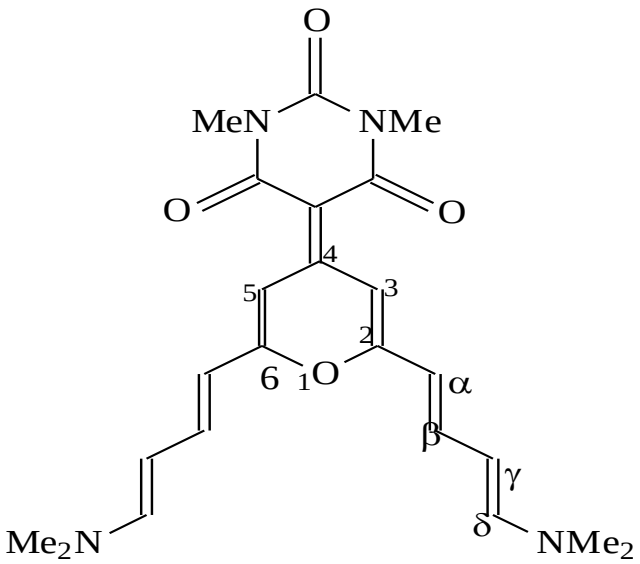
.

Table S6 ^{1}H-^{1}H and ^{1}H-^{13}C correlation data in NOESY and HMBC experiments (DMSO-d_6) for polyene **13c.**



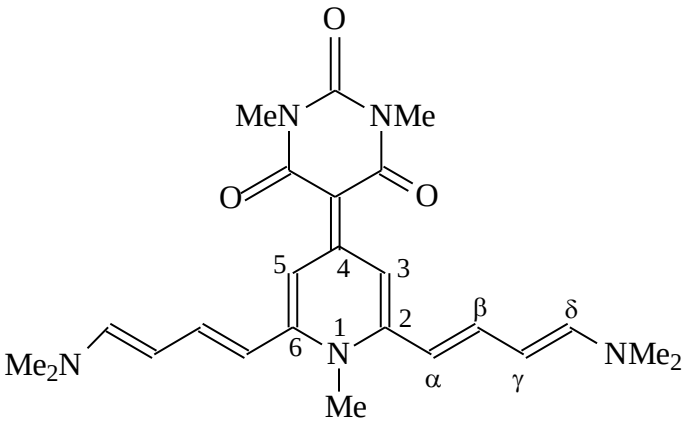
Atom	ROESY, H	HMBC, C
C(3)H, C(5)H	H(β)	C(α), C(2), C(6)
H(α)	H(γ), NMe	C(3), C(5), C(γ), C(β)
H(β)	H(3), H(5), H(δ)	C(δ), C(2), C(6)
H(γ)	H(α), NMe_2	C(α), C(β), C(δ)
H(δ)	H(β), NMe_2	C(γ), (Cβ), NMe_2
NMe_2	H(γ), H(δ)	C(δ)
NMe	H(α)	C(2), C(6)

Table S7 ^{1}H-^{1}H correlation data in NOESY experiments (DMSO-d_6) for polyene **12d.**



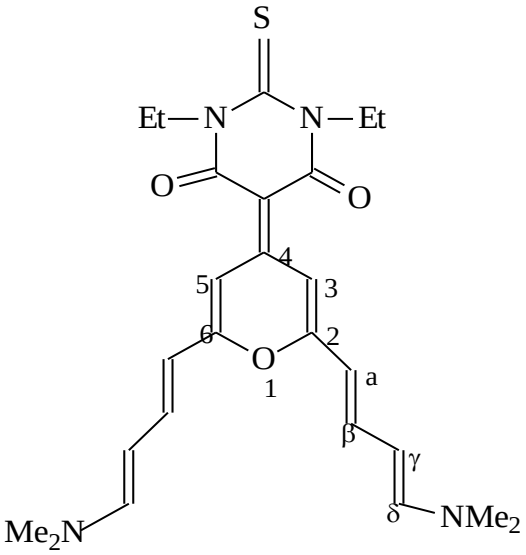
Atom	NOESY
H(α)	H(γ), H(3), H(5)
H(β)	H(δ)
H(γ)	H(α), NMe_2
H(δ)	H(β), NMe_2
NMe_2	H(δ)
C(3)H, C(5)H	H(α)

Table S8 ^{1}H-^{1}H correlation data in ROESY experiments (DMSO-d_6) for polyene **13d.**



Atom	ROESY
H(α)	H(γ), NMe
H(β)	H(3), H(5), H(δ)
H(γ)	H(α), NMe_2
H(δ)	NMe_2, H(β)
NMe_2	H(γ), H(δ)
NMe	H(α)
C(3)H, C(5)H	H(β)

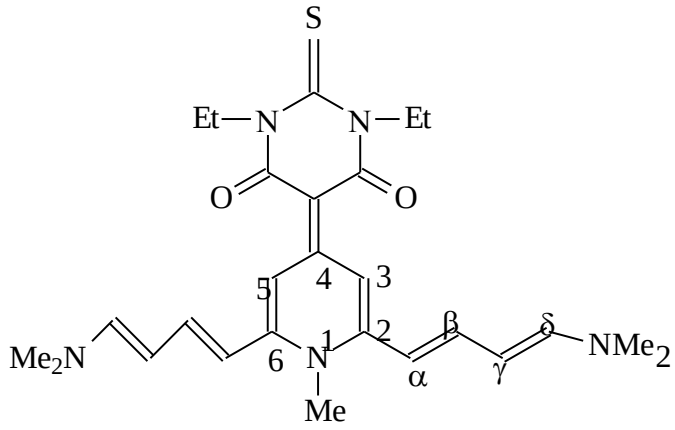
Table S9 ^{1}H-^{1}H and ^{1}H-^{13}C correlation data in NOESY and HMBC experiments (DMSO-d_6) for polyene **12e.**



Atom	NOESY, H	HMBC, C
H(α)	H(3)*, H(5)*	C(γ), C(2), C(6), C(3), C(5)
H(β)	-	C(δ), C(2), C(6)
H(γ)		C(α)
H(δ)		C(β), C(γ), NMe_2
NMe_2		C(δ)
C(3)H, C(5)H	H(α)*	C(α), C(2), C(6)

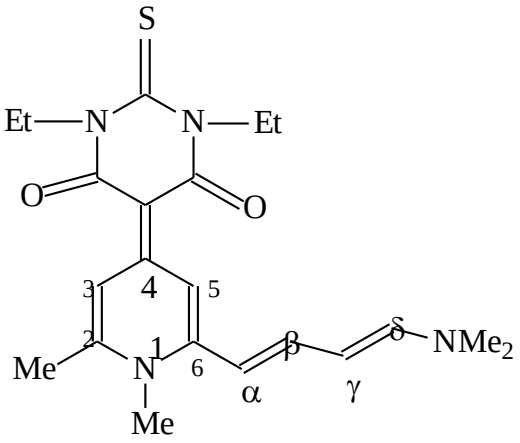
*Based on NOE experiment in 1 D ROESY.

Table S10 ^{1}H-^{1}H correlation data in ROESY experiments (DMSO-d_6) for polyene **13e.**



Atom	ROESY, H
H(α)	NMe, H(γ)
H(β)	H(3), H(5), H(δ)
H(γ)	NMe_2, H(α)
H(δ)	NMe_2, H(β)
NMe	H(α)
NMe_2	H(γ), H(δ)
C(3)H, C(5)H	H(β)

Table S11 ^{1}H-^{1}H correlation data in ROESY experiments (DMSO-d_6) for tetraene **14.**



Atom	ROESY, H
H(α)	H(γ), NMe
H(β)	H(5)
H(γ)	H(α), NMe_2
H(δ)	NMe_2
NMe_2	H(γ), H(δ)
NMe	H(α)
C(2)Me	H(3), NMe
C(5)H	H(β)