Spectral and fluorescent properties of cross-conjugated polyene ketones with terminal *N*-methylpyrrole residues

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The spectral and fluorescent properties of a number of cross-conjugated ketones with one or two terminal *N*-methylpyrrole residues and those of polyene bis-ω,ω′-dimethylamino ketones with methyl substituents in the polyene chain and of some related compounds were studied. The photophysical properties of cross-conjugated ketones with terminal *N*-methylpyrrole residues are similar to those of the corresponding polyene bis-ω,ω′-dimethylamino ketones studied in detail previously. In both series of compounds, the absorption and fluorescence spectra undergo a bathochromic shift following an increase in the length of the polyene chains or introduction of α,α′-trimethylene or α,α′-dimethylene bridges into these chains; the same trend is observed on passing from less polar solvents to more polar solvents (positive solvatochromism). Thermochromism (long-wavelength shift of the absorption spectra upon cooling the solutions) is observed in both series of compounds. The introduction of methyl substituents into the polyene chains of bis-ω,ω′-dimethylamino ketones results in a decrease in the fluorescence quantum yield.

Key words: absorption and fluorescence spectra, solvatochromism, thermochromism, cross-conjugated polyene ketones, *N*-methylpyrroles.

This study is devoted to spectral-fluorescent properties of cross-conjugated ketones containing an *N*-methylpyrrole ring in the β- or β- and β′-positions.

Recently, we prepared these previously unknown compounds (Table 1) by condensation of 1,3-bis(dimethylamino)-2-[dimethylamino(methoxy)methyl]-1-methoxyprop-2-ene[1] (**1**) with various ketones, which was accompanied by an unusual intramolecular cyclization[2,3] to give asymmetrical (**2**—**10**) or symmetrical (**11**—**13**) ketones (Scheme 1).

The interest in the spectroscopic properties of cross-conjugated ketones **2**—**13** is due to the fact that their analogs, α,α′-bis(ω-dimethylaminopolyenyl) ketones (BDAK), prepared previously, which also contain two chromophores interacting *via* a carbonyl group, possess a number of specific properties such as clear-cut solvatochromism,[4] thermochromism,[5] fluorescence, and generation of laser radiation.[6]

In the present study, we measured the absorption and fluorescence spectra and, in some cases, the fluorescence quantum yields (φ_{fl}) of cross-conjugated ω-dimethylamino ketones containing a terminal *N*-methylpyrrole ring (**2**—**10**), ketones with two terminal *N*-methylpyrrole rings (**11**—**13**), new polyene BDAK **14** and **15**, tris(dimethylamino) diketone **16**,[3] and triene dimethylamino ketone **17**, whose structural formulas are presented in Table 1. For comparison, the spectra of cross-conjugated BDAK with a nonbranched chain,

Scheme 1

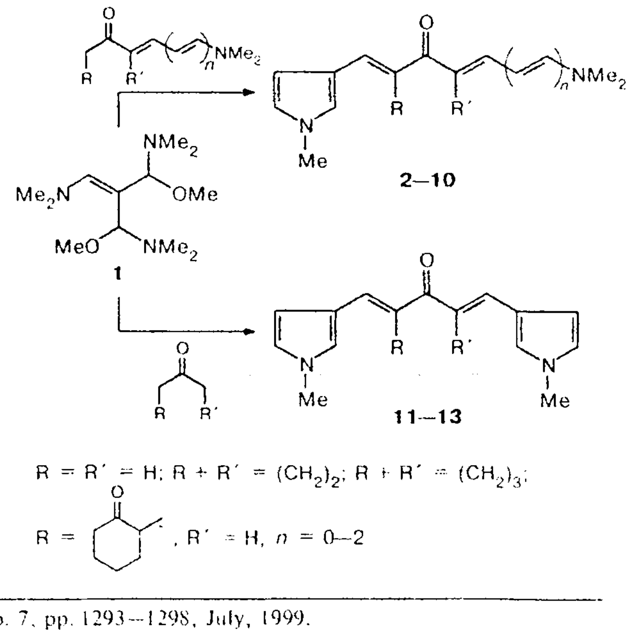

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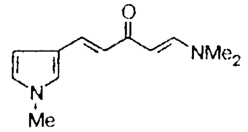
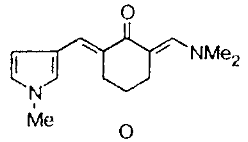
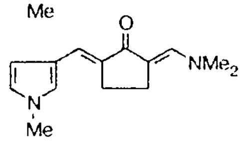
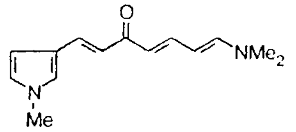
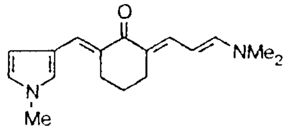
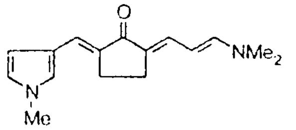
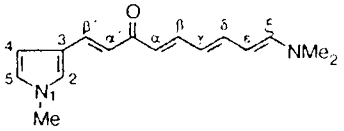
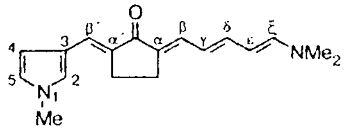
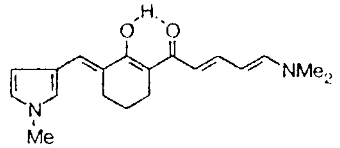
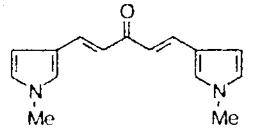
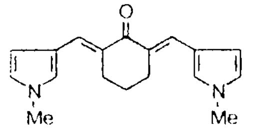
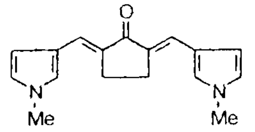
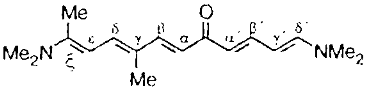
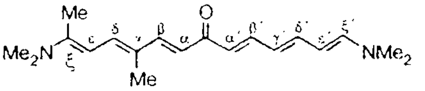
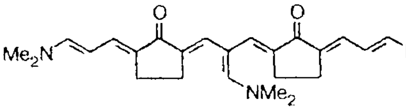
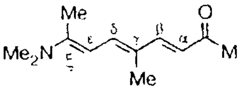
Table 1. Absorption and fluorescence spectra and fluorescence quantum yields (φ_{fl}) for **2**—**17**

Compound	λ^{abs}_{max}/nm (ε)			λ^{fl}_{max}/nm (φ_{fl})	
	EtOH	Pr^{i}OH	Toluene	Pr^{i}OH	Toluene
 (**2**)	375 (32000)	370	352	435	—
 (**3**)	395 (36000)	390	365	466	—
 (**4**)	405 (54000), 415 sh (46000)	399	380	440, 460	~445
 (**5**)	448 (47000)	437	405	506 (0.024)	474
 (**6**)	450 (100000)	446	415	518	475
 (**7**)	474 (118000)	465	439	518 (0.066)	483
 (**8**)	480 (50000)	475	448	596 (0.10)	535
 (**9**)	510 (51200)	507	465	604 (0.064)	536
 (**10**)	486 (93000)	483	469	558 (0.12)	530 (0.068)
 (**11**)	386 (40000)	385	363	476	weak
 (**12**)	400 (53000)	391	367	~466	—

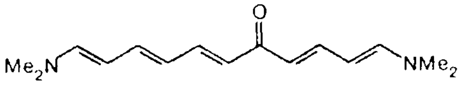
(to be continued)

Table 1 (*continued*)

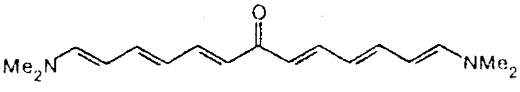
Compound	λ^{abs}_{max}/nm (ε)			λ^{fl}_{max}/nm (φ_{fl})	
	EtOH	Pr^{i}OH	Toluene	Pr^{i}OH	Toluene
 (**13**)	400 sh (47000), 410 (57000)	396	395	438, 459	weak
 (**14**)	417 sh (18700), 528 (72300)	504, 513^b	462	610, 622^b (0.24)^b	535
 (**15**)	440 sh (45300), 530 (131800)^a	543, 550^b	486	648, 654^b (0.084)^b	561
 (**16**)	480 (57000)	481	442	518 (0.0075)	477
 (**17**)	457 (45800)	443	419	~525 (weak)	–

^{a} In CH_2Cl_2.
^{b} In Pr^{n}OH.

1,1-bis(dimethylamino)undeca-1,3,6,8,10-pentaen-5-one (**18**)[4] and 1,13-bis(dimethylamino)trideca-1,3,5,8,10,12-hexaen-7-one (**19**),[4] were also studied. Ketones **8** and **9** were first obtained in this work by the reaction of compound **1** with amino ketones **20** and **21**.



18



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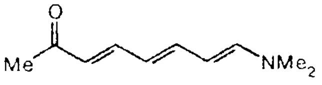
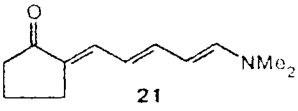


20



21

Experimental

The absorption spectra of the studied compounds were recorded on a Specord UV VIS spectrophotometer, and the fluorescence spectra were measured on an Aminco-Bowman spectrofluorimeter with an R136 photomultiplier. The fluorescence spectra were not corrected for the spectral sensitivity of the spectrofluorimeter. To determine fluorescence quantum yields (φ_{fl}) for compounds **5—7** and **16** (in Pr^{i}OH) and for **9** (in toluene), a 10^{-6} *M* alkaline aqueous solution of fluorescein (φ_{fl} = 0.85) was used as the standard,[6] for compounds **8—9** (in Pr^{i}OH), a 10^{-6} *M* solution of Rhodamine B in ethanol (φ_{fl} = 0.65) was used,[7] and for compounds **14**, **15**, **18**, and **19** (in Pr^{i}OH), an asymmetrical cyanine dye, indobenzimidazolodicarbocyanine, in acetonitrile (φ_{fl} = 0.07) was employed.[8] ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in relation to Me_4Si. Mass spectra (EI, *m/z*, I_{rel} (%)) of compounds **8**, **9**, and **17** were run on an MS-30 instrument (70 eV), and those for compounds **14** and **15** were measured on a Jeol JMS-D-300 instrument (70 eV).

Triene ketones 20 and 21 were prepared by a previously described procedure.[9] The too small amounts of the initial compounds and the low yields of the products precluded the use of elemental analysis for identification of compounds **8**, **9**, **14**, **15**, and **17**.

2-[5-(Dimethylamino)penta-2,4-dienylidene]-5-(*N*-methylpyrrol-3-yl)methylenecyclopentanone (9). A mixture of acetal aminal **1** (0.43 g, 1.6 mmol) and 2-[5-(dimethylamino)penta-2,4-dienylidene]cyclopentanone (0.15 g, 0.79 mmol) (**21**) was heated for 35 min at 65—70 °C. The resulting thick oil was dissolved in 25 mL of CH_2Cl_2, and 2 g of silica gel (40/100) was added to the solution. After 16 h, SiO_2 was filtered off and washed with CH_2Cl_2 and the filtrate was concentrated. The semicrystalline precipitate was washed with anhydrous ether, then heptane was added, the mixture was cooled to −10 °C, and the precipitate was triturated. The crystals were filtered off and washed with anhydrous ether and heptane. Washing with hot acetone gave 30 mg (14%) of compound **9** as vinous-colored crystals, m.p. 203—206 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.80 (m, 4 H, CH_2); 2.88 (s, 6 H, NMe_2); 3.70 (s, 3 H, NMe); 6.04 (t, 1 H, γ-H, $J_{\beta,\gamma} = J_{\gamma,\delta} = 13.0$ Hz); 6.40 (br.s, 1 H, H-4); 6.63 (br.s, 1 H, H-5); 6.70 (t, 1 H, δ-H, $J_{\gamma,\delta} = J_{\delta,\varepsilon} = 13.0$ Hz); 6.90 (br.s, 1 H, H-2); 7.20 (d, 1 H, β-H, $J_{\beta,\gamma} = 13.0$ Hz); 7.40 (br.s, 1 H, β′-H). MS, *m/z*: 282 $[M]^+$ (71.9%), 267 $[M - Me]^+$ (11.8%), 237 $[M - NHMe_2]^+$ (13.7%), 208 $[M - NHMe_2 - CH_2]^+$ (20%), 118 (100%), 81 $[N\text{-methylpyrrole}]^+$ (23.6%).

1-(*N*-Methylpyrrol-3-yl)-9-(dimethylamino)nona-1,4,6,8-tetraen-3-one (8) was prepared in a similar way from compound **1** and 8-(dimethylamino)octa-3,5,7-trien-2-one (**20**). To isolate compound **8**, the residue obtained after evaporation of CH_2Cl_2 was triturated in anhydrous ether, and the crystals were separated and washed with anhydrous ether. Yield 30%, m.p. 155—159 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.88 (s, 6 H, NMe_2); 3.66 (s, 3 H, NMe); 5.15 (dd, 1 H, ε-H, $J_{\delta,\varepsilon} = 14.2$ Hz, $J_{\varepsilon,\xi} = 12.9$ Hz); 6.06 (dd, 1 H, γ-H, $J_{\beta,\gamma} = 12.9$ Hz, $J_{\gamma,\delta} = 10.3$ Hz); 6.23 (d, 1 H, α-H, $J_{\alpha,\beta} = 15.5$ Hz); 6.41 (t, 1 H, H-4, $J_{4,5} = 2.5$ Hz); 6.59 (t, 1 H, H-5, $J_{2,5} = J_{4,5} = 2.5$ Hz); 6.62 (dd, 1 H, δ-H, $J_{\gamma,\delta} = 10.3$ Hz, $J_{\delta,\varepsilon} = 14.2$ Hz); 6.64 (d, 1 H, α′-H, $J_{\alpha',\beta'} = 15.5$ Hz); 6.86 (t, 1 H, H-2, $J_{2,5} = 2.5$ Hz); 7.42 (dd, 1 H, β-H, $J_{\alpha,\beta} = 15.5$ Hz, $J_{\beta,\gamma} = 12.9$ Hz); 7.58 (d, 1 H, β′-H, $J_{\alpha',\beta'} = 15.5$ Hz). MS, *m/z*: 256 $[M]^+$ (7.5%), 211 $[M - Me_2NH]^+$ (47.5%), 176 $[M - N\text{-methylpyrrolyl}]^+$ (40%), 134 (100%), 80 $[N\text{-methylpyrrolyl}]^+$ (30%).

8-Dimethylamino-5-methylnona-3,5,7-trien-2-one (17). A mixture of [8-(*N*,*N*-dimethylamino)-5-methylnona-3,5,7-trienylidene]-2-*N*,*N*-dimethylimmonium iodide (0.9 g, 2.6 mmol),[10] finely powdered potassium carbonate (0.9 g), 15 mL of ether, and 2.5 mL of MeOH was stirred for 4 days at 20 °C. Finely powdered KOH (0.1 g) was added and the mixture was stirred for an additional 24 h. The solution was filtered off and concentrated. An ether—heptane (1 : 1) mixture was added to the solid residue and the mixture was filtered off to give 300 mg (60%) of compound **17** as a red-brown precipitate with metallic luster, m.p. 100—103 °C. ^{1}H NMR ($CDCl_3$), δ: 1.81 (s, 3 H, Me); 2.09 (s, 3 H, Me); 2.24 (s, 3 H, CO—$\underline{Me}$); 2.96 (s, 6 H, NMe_2); 5.19 (d, 1 H, ε-H, $J_{\delta,\varepsilon} = 10.4$ Hz); 5.95 (d, 1 H, α-H, $J_{\alpha,\beta} = 15$ Hz); 6.78 (d, 1 H, δ-H, $J_{\delta,\varepsilon} = 10.4$ Hz); 7.31 (d, 1 H, β-H, $J_{\alpha,\beta} = 15$ Hz). MS, *m/z*: 193 $[M]^+$ (35%), 178 $[M - Me]^+$ (14.6%), 150 $[M - MeCO]^+$ (100%), 136 $[M - MeCO - CH_2]^+$ (12.3%).

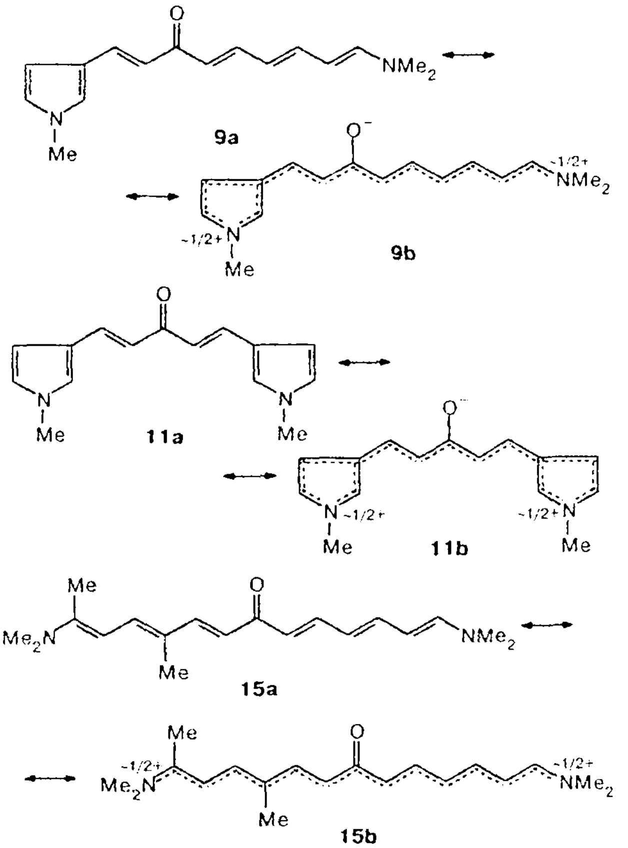
1,11-Bis(dimethylamino)-8-methyldodeca-1,3,5,8,10-pentaen-5-one (14). A mixture of β-dimethylaminoacrolein aminal (0.16 g, 1 mmol)[11] and ketone **17** (0.2 g, 1 mmol) was heated at 60 °C for 15 min. The resulting crystalline mixture was diluted with dry acetone and triturated, and the precipitate was filtered off and washed with anhydrous acetone and then with anhydrous ether to give 150 mg (53%) of a lilac precipitate, m.p. 193—197 °C. ^{1}H ($CDCl_3$), δ: 1.86 (s, 3 H, Me); 2.06 (s, 3 H, Me); 2.83 (s, 6 H, NMe_2); 2.93 (s, 6 H, NMe_2); 5.21 (m, 2 H, γ′-H and ε-H); 6.13 (m, 2 H, α-H and α′-H); 6.73 (m, 2 H, δ-H and δ′-H); 7.43 (d, 1 H, β-H, $J_{\alpha,\beta} = 16.0$ Hz); 7.45 (dd, 1 H, β′-H, $J_{\alpha',\beta'} = 12.2$ Hz, $J_{\beta',\gamma'} = 15.1$ Hz). MS, *m/z*: 247 $[M]^+$ (24%), 229 $[M - Me_2NH]^+$ (23.2%), 214 $[M - Me_2N - Me]^+$ (12.5%), 193 $[M - Me_2NH - C_3H_2]^+$ (19.6%), 150 $[M - Me_2NC_3H_2 - MeCO]^+$ (89.3%), 145 $[M - 2\ Me_2N - Me - C_2H_2]^+$ (100%).

1,13-Bis(dimethylamino)-10-methyltetradeca-1,3,5,8,10,12-hexaen-7-one (15). A mixture of ketone **17** (0.15 g, 0.78 mmol) and 5-dimethylamino-2,4-pentadienal aminal (0.15 g, 0.78 mmol)[12] was heated at 65—80 °C for 45 min. Anhydrous ether was added to the reaction mixture, the resultant mixture was cooled to 20 °C, and the precipitate was triturated and filtered off. The precipitate was suspended in dry acetone, and the insoluble part was separated and washed with dry acetone and anhydrous ether to give 40 mg (17%) of compound **15** as dark-grey crystals, m.p. 173—177 °C. ^{1}H NMR ($CDCl_3$), δ: 1.81 (s, 3 H, Me); 2.07 (s, 3 H, Me); 2.85 (s, 6 H, NMe_2); 2.96 (s, 6 H, NMe_2); 5.07—5.23 (m, 2 H, ε-H and ε′-H); 6.05 (t, 1 H, γ′-H, $J_{\beta',\gamma'} = 14.3$ Hz); 6.20 (m, 2 H, α-H and α′-H); 6.50 (d, 1 H, ξ′-H, $J_{\varepsilon',\xi'} = 14.3$ Hz); 6.62 (t, 1 H, δ′-H, $J_{\gamma',\delta'} = J_{\delta',\varepsilon'} = 14.3$ Hz); 6.89 (d, 1 H, δ-H, $J_{\delta,\varepsilon} = 12.0$ Hz); 7.39 (t, 1 H, β′-H, $J_{\alpha',\beta'} = J_{\beta',\gamma'} = 14.3$ Hz); 7.48 (d, 1 H, β-H, $J_{\alpha,\beta} = 14.3$ Hz). MS, *m/z*: 300 $[M]^+$ (5%), 255 $[M - Me_2NH]^+$ (20%), 193 $[M - Me_2N - C_5H_3]^+$ (15%), 150 $[M - Me_2N - C_5H_3 - MeCO]^+$ (100%), 122 (24%).

Results and Discussion

The photophysical properties of cross-conjugated ketones **2**—**13** with terminal *N*-methylpyrrole rings resemble those of the previously studied[6,13] series of BDAK (including compounds **14** and **15** synthesized in this study). For both series of compounds, the absorption and fluorescence bands shift bathochromically as the polyene chain becomes longer and when an α,α′-trimethylene or α,α′-dimethylene bridge is introduced into the molecule (in the latter case, the shifts are especially pronounced, *cf.* amino ketones **2**, **3**, and **4**; **5**, **6**, and **7**; **8** and **9**; **11**, **12**, and **13**); the same is observed on going from less polar solvents to more polar ones (positive solvatochromism). Comparison of the absorption spectra (in Pr^{i}OH) of ketones **2**—**13** with those of BDAK with the same length of the polyene chain (without allowance for the pyrrole fragment) shows that the replacement of the amino group in BDAK by an *N*-methylpyrrole fragment causes a bathocromic shift of the spectra, equal to 7—25 nm. Both classes of compounds display relatively large Stokes shifts of the fluorescence spectra (60—120 nm), and the fluorescence quantum yields in polar (especially in proton-donor) solvents are much higher than those in nonpolar solvents. This is due to solvation of the carbonyl group and the formation of a hydrogen bond between this carbonyl group and a proton-donor solvent, resulting in the π-electron system of the polymethine chain of the amino ketone (structure **a**) being brought closer to mesomeric bipolar structure **b**, responsible for a longer-wavelength absorption spectrum[5] (Scheme 2).

Scheme 2



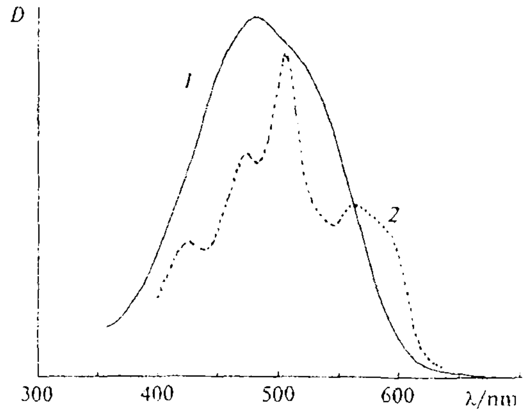


Fig. 1. Absorption spectra of dye **16** in Pr^{i}OH at 290 (*1*) and 90 K (*2*).

Cross-conjugated ketones **2**—**4** and **11**—**13** with *N*-methylpyrrole rings and short polymethine chains (one —CH=CH— on each side), like BDAK with short chains, are characterized by low φ_{fl} values (<0.01). As the polymethine chains become longer (compounds **5**—**10**), the fluorescence quantum yields increase. The large Stokes shifts combined with high fluorescence quantum yields make compounds **7**—**10**, **14**, and **15** promising for the generation and transformation of laser radiation. Amino ketone **10** exhibits a fairly high fluorescence quantum yield both in polar and nonpolar solvents, which is due to the interaction of the carbonyl group with the β-hydroxy group leading to an intramolecular hydrogen bond.

The fluorescence quantum yields for dimethyl-substituted BDAK **14** and **15** are substantially lower than those for the corresponding unsubstituted BDAK **18** and **19** (see Table 1). This can be explained by assuming that upon substitution, the rate of nonradiative deactivation of the excited singlet state of BDAK increases due to the participation of the vibrational degrees of freedom of substituents (especially, the anharmonic C—H vibrations of the methyl groups).

For a number of ketones studied, thermochromism is observed, *i.e.*, absorption spectra undergo a long-wavelength absorption shift following a decrease in temperature, which has been observed in our earlier studies of analogous compounds.[5,14] In particular, a large thermochromic shift has been observed for amino ketone **8**: the maximum of its absorption spectrum recorded in Pr^{n}OH shifts from 470 nm at 351 K to 529 nm at 140 K (2370 cm^{-1}). When a solution of compound **8** in a toluene—3-methylpentane mixture (1 : 2) is cooled from 347 to 152 K, this shift is 2600 cm^{-1} (from 419 to 471 nm). The thermochromic shift occurring on cooling of a solution of **15** in Pr^{n}OH from 349 to 161 K is also fairly large (2140 cm^{-1}); that observed in a toluene—3-methylpentane mixture (1 : 2) on cooling from 345 to 153 K is 2060 cm^{-1}. Cooling of solutions of compounds **10** and **16** in Pr^{i}OH from room temperature to 90 K results in thermochromic shifts equal to 1000 and 1200 cm^{-1}, respectively. It should be noted that cooling of a solution of polyene tris(dimethylamino) diketone **16** in Pr^{i}OH leads to resolution of the absorption spectrum structure to give four bands, resulting from interaction of four polyene chromophores in **16** (Fig. 1).

Cooling of solutions of the compounds studied in 3-methylpentane induces large thermochromic changes in absorption spectra; however, our studies showed that these changes are due to aggregation of amino ketones to give species that are responsible for long-wavelength absorption rather than to the displacement of the spectra of the monomeric species. In this case, changes in the absorption spectra can be very large (about 5000 cm^{-1}).

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References

1. Zh. A. Krasnaya, Yu. V. Smirnova, G. V. Krystal, and V. S. Bogdanov, *Mendeleev Commun.*, 1996, 17.
2. Zh. A. Krasnaya, Yu. V. Smirnova, and V. S. Bogdanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 785 [*Russ. Chem. Bull.*, 1996, **45**, 745 (Engl. Transl.)].
3. Zh. A. Krasnaya, Yu. V. Smirnova, and V. S. Bogdanov, *Khim. Geterotsikl. Soedinen.*, 1996, 654 [*Chem. Heterocyclic. Compd.*, 1996 (Engl. Transl.)].
4. Zh. A. Krasnaya, T. S. Stytsenko, B. M. Uzhinov, S. A. Krashakov, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2084 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1882 (Engl. Transl.)].
5. L. A. Shvedova, A. S. Tatikolov, V. A. Kuz'min, Zh. A. Krasnaya, and A. R. Bekker, *Dokl. Akad. Nauk SSSR*, 1984, **276**, 654 [*Dokl. Phys. Chem.*, 1984, **276**, 457 (Engl. Transl.)].
6. L. A. Shvedova, A. S. Tatikolov, A. P. Darmanyan, V. A. Kuz'min, and Zh. A. Krasnaya, *Dokl. Akad. Nauk SSSR*, 1984, **276**, 164 [*Dokl. Phys. Chem.*, 1984, **276** (Engl. Transl.)].
7. C. A. Parker, *Photoluminescence of Solutions*, Elsevier Publ. Co., Amsterdam, 1968].
8. R. F. Kubin and A. N. Fletcher, *J. Luminescence*, 455, 27, 1982.
9. Zh. A. Krasnaya and T. S. Stytsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 855 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 780 (Engl. Transl.)].
10. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 123 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 107 (Engl. Transl.)].
11. Zh. A. Krasnaya, T. S. Stytsenko, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 106 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 96 (Engl. Transl.)].
12. Zh. A. Krasnaya and T. S. Stytsenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 850 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 776 (Engl. Transl.)].
13. L. A. Shvedova, Yu. E. Borisevich, A. S. Tatikolov, V. A. Kuz'min, and Zh. A. Krasnaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 819 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 747 (Engl. Transl.)].
14. A. S. Tatikolov, N. A. Derevyanco, A. A. Ishcenco, I. Baraldi, V. Caselli, F. Momicchioli, and G. Ponterini, *Ber. Bunsenges. Phys. Chem.*, 1995, **99**, 763.

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