Synthesis and spectroscopic and structural studies of cross-conjugated dienones derived from cyclic ketones and aromatic aldehydes

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Cross-conjugated dienones were synthesized by the reactions of cyclic ketones with two equivalents of aromatic aldehydes under basic conditions. An NMR spectroscopic study and X-ray diffraction analysis demonstrated that all reaction products are formed as *E*,*E* isomers. Spontaneous photochemical *trans—cis* isomerization of cross-conjugated dienones under the scattered light in solution was observed for the first time. The degree of isomerization depends mainly on the nature of the central fragment of the dienone molecule. The previously unknown product of photochemical [2+2]-cycloaddition of 2,5-bis[(*E*)-(3-pyridyl)methylidene]cyclopentanone was synthesized and characterized by spectroscopic methods and X-ray diffraction. Under the conditions used, only one isomer of the cyclobutane adduct was obtained.

Key words: cross-conjugated dienones, ketones, aromatic aldehydes, X-ray diffraction analysis, photoisomerization, [2+2]-cycloaddition.

Cross-conjugated dienones of the bis-arylidenecycloalkanone series (hereinafter, dienones) are generally synthesized by the reactions of cyclic ketones with two equivalents of aromatic aldehydes. These compounds are used for the construction of polymers,[1,2] crystals with the nonlinear optical properties,[3—5] and dyes,[6] as well as for the synthesis of numerous condensed systems based on hydrazine, thioureas, cyanoacetamide, guanidine derivatives, and many other compounds.[7—12] Both dienones and their heterocyclization products have various biological activities, such as antiviral,[11] antimicrobial,[13,14] and anti-inflammatory[15,16] activities, and can be used as anesthetics,[17] cholagogues,[18] and contraceptives.[19]

The dienone derivatives of cyclopentanone, cyclohexanone, and cycloheptanone have been synthesized and reliably characterized. Substituted benzaldehydes containing chlorine, bromine, methyl, methoxy, phenoxy, and/or nitro groups in different positions of the benzene ring of aldehydes, as well as heteroaromatic 2-thiophene- and 2-furanaldehydes, were used as the aldehyde component. Dienones derived from *N*-methyl- and *N*-butyl-4-piperidones and tropanones are much less in number. The synthesis of tropanone derivatives based on 4- and 3-pyridinealdehydes was documented.[18]

Recently,[20] it has been suggested to use pyridine-containing dienones as exodentate ligands, which can react with metal ions to form so-called coordination polymers, *viz.*, infinite ensembles $(M—L)_n$ (M is metal and L is ligand). In the present study, we examined a series of pyridine- and thiophene-containing bis-arylidene deriva-

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tives of cycloalkanones suitable for the preparation of supramolecular complexes. In addition, dienones based on substituted benzaldehydes were studied as model compounds. Some of these compounds were described in the literature. However, in most cases, no spectroscopic, stereochemical, and photochemical studies were performed.

Results and Discussion

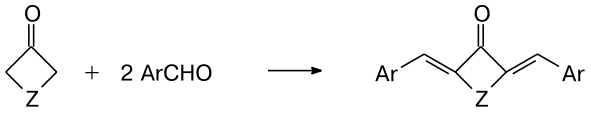
In the present study, we performed aldol-crotonic condensation of carbocyclic cyclopentanone and cyclohexanone and heterocyclic 1-methyl-, 1-benzyl-, 1-ethyl-, and 1-isopropyl-4-piperidones with aromatic and heteroaromatic aldehydes. Several methods have been developed for performing this reaction, which differ in the nature of the catalyst and the solvent. The classical method is based on condensation of ketones and aldehydes in an alcoholic or aqueous medium in the presence of a base.[21—27] Acetic acid in the presence of HCl was used only for the synthesis of dienones from *N*-butylpiperidone.[18] In recent years, transition metal-based catalysts, for example, Cp_2ZrCl_2 in the presence of $NiCl_2$,[28] $TiCl_3(SO_3CF_3)$ under solvent-free conditions,[29] $RuCl_3$ in a sealed tube under solvent-free conditions,[30] and in ionic liquids in the presence of $FeCl_3 \cdot 6H_2O$ (see Ref. 31), have found use. It should be noted that not nearly all of the above-mentioned conditions are suitable for the reactions with heteroaromatic, particularly, pyridine aldehydes. In the present study, we used basic catalysis in aqueous[6] or aqueous-alcoholic[21] media as the simplest and most universal conditions.

Dienones were synthesized according to Scheme 1.

Generally, condensation occurs in good yield. For example, the reactions with 2-thiophenecarbaldehyde produce dienone derivatives in yields from 64 to 96%. 4-Dimethylaminobenzaldehyde proved to be least reactive. The reactions with the latter compound afforded target products in yields of, at most, 30% because it was accompanied by polymerization. The reactions with 1-methyl-4-piperidone also proceeded with difficulty. We failed to prepare products of its condensation with 2-furancarbaldehyde and 2-furan-5-methylcarbaldehydes. The lower reactivity of 1-methyl-4-piperidone in such reactions compared to cyclohexanone is unlikely to be attributed exclusively to the inclusion of the heteroatom into the carbocycle because related 1-benzyl-4-piperidone is reactive under analogous conditions and is involved in condensation with all used aldehydes to form the corresponding dienones.

The structures of the resulting condensation products were established by ^1H and ^{13}C NMR and IR spectroscopy. The IR spectra of all compounds show two characteristic bands in the 1720—1670 and 1620—1590 cm^{-1} regions, which is indicative of the presence of the carbonyl group conjugated with the double bonds. This is also

Scheme 1



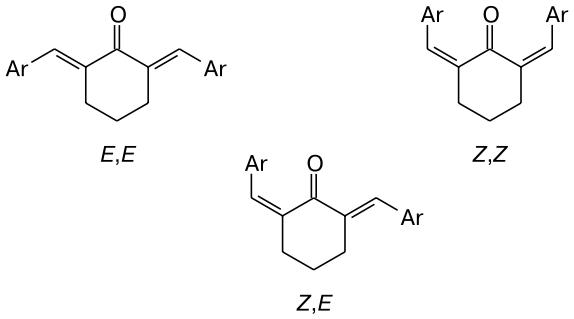
1—32

Z	Ar	Product	Yield (%)
$(CH_2)_2$	Ph	**1**	87
	$4\text{-}MeOC_6H_4$	**2**	65
	$4\text{-}MeNC_6H_4$	**3**	25
	2-Fur[a]	**4**	88
	2-Th[b]	**5**	96
	4-Py[c]	**6**	50
	3-Py	**7**	73
	2-Py	**8**	69
$(CH_2)_3$	Ph	**9**	90
	$4\text{-}MeOC_6H_4$	**10**	38
	2-Fur	**11**	60
	5-Me(C_4H_2O)[d]	**12**	68
	2-Th	**13**	86
	4-Py	**14**	98
	3-Py	**15**	76
$CH_2N(Me)CH_2$	Ph	**16**	50
	$4\text{-}MeOC_6H_4$	**17**	44
	$4\text{-}MeNC_6H_4$	**18**	16
	2-Th	**19**	64
	4-Py	**20**	68
	3-Py	**21**	50
$CH_2N(Ph)CH_2$	Ph	**22**	51
	$4\text{-}MeOC_6H_4$	**23**	48
	$4\text{-}Me_2NC_6H_4$	**24**	18
	2-Fur	**25**	78
	5-Me(C_4H_2O)	**26**	82
	2-Th	**27**	90
	4-Py	**28**	50
	3-Py	**29**	37
	2-Py	**30**	75
$CH_2N(Et)CH_2$	3-Py	**31**	33
$CH_2N(Pr^i)CH_2$	3-Py	**32**	30

[a] Fur is furyl. [b] Th is thienyl. [c] Py is pyridyl.
[d] 5-Methylfuran-2-yl.

confirmed by the chemical shifts of the carbonyls in the ^{13}C NMR spectra ($\delta \approx 190$).

Dienone derivatives of cyclic ketones can exist in *E*,*E*, *Z*,*Z*, or *Z*,*E* configurations.



In all reactions, we obtained only the *E*,*E* isomer. In the spectra of all compounds, the signals for the protons

of the CH= group appear at δ 7.30—7.90. It is known[32] that the *Z* isomers are characterized by the chemical shifts at δ ~6.8, whereas the signals for the *E* isomers should appear at higher field than 7.2 ppm.

The structures of compounds **6**, **13**, **14**, and **31** were additionally confirmed by X-ray diffraction (Table 1, Table 2, Fig. 1). The structure of compound **15** has been established earlier.[20] It should be noted that data on the structures of dienones containing heterocyclic substituents are lacking in the literature.

A common structural feature of pyridine-containing molecules is the presence of the following three planar fragments: the central dienone group including the oxygen and carbon atoms of the carbonyl group and the carbon atoms of the adjacent double bonds (hereinafter denoted as Cen) and two heterocyclic fragments including six atoms of the pyridine ring (hereinafter denoted as Het^1 and Het^2). The dihedral angles between the corresponding mean planes and the lengths of the double bonds (C=C and C=O) and the adjacent bonds are given in Table 2.

Cyclopentane dienone molecule **6** is rather planar unlike the six-membered analogs, in which the presence of the additional methylene or *N*-alkylamino group causes the deviation of the latter from the plane formed by three trigonal and two methylene carbon atoms of the ring.

In the recent study[33] concerned with the nonlinear optical properties of crystals of dibenzylidenecycloalkanones, it has been demonstrated that the intermolecular C—H...O bond (or several such bonds) between the carbonyl oxygen atom and the hydrogen atom of the methylene group is an important factor responsible for the crystal structure of these compounds. Among the crystals under study, the shortest C—H...O contact (2.42(1) Å) was found in the structure of cyclopentanone derivative **6**. As in the structure of phenyl analog **1**,[33] the oxygen atom

Table 1. Crystallographic data, details of X-ray data collection, and characteristics of the structure refinement of compounds **6**, **13**, **14**, **31**, and **33**

Compound	**6**	**13**	**14**	**31**	**33**
Molecular formula	$C_{17}H_{14}N_2O$	$C_{16}H_{14}OS_2$	$C_{18}H_{16}N_2O$	$C_{19}H_{19}N_3O$	$C_{35.50}H_{28.39}Cl_6N_4O_{2.19}$
Molecular weight	262.30	286.39	276.33	305.37	758.83
Crystal dimensions/mm	0.40×0.20×0.20	0.30×0.20×0.20	0.50×0.40×0.40	0.40×0.20×0.20	0.20×0.10×0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	6.0078(2)	15.000(9)	8.309(9)	6.010(5)	13.2251(4)
b/Å	11.6896(4)	11.982(8)	9.261(5)	8.942(2)	15.9387(4)
c/Å	18.5325(6)	7.608(7)	18.824(15)	15.190(7)	16.9422(5)
α/deg	90	90	90	98.30(3)	83.847(1)
β/deg	95.807(1)	95.87(6)	100.94(8)	97.97(5)	79.893(2)
γ/deg	90	90	90	98.60(5)	79.163(1)
V/Å^3	1294.84(7)	1360(2)	1422(2)	787.9(8)	3443.0(2)
Z	4	4	4	2	4
d_{calc}/g cm^{-3}	1.346	1.398	1.290	1.287	1.464
μ/mm^{-1}	0.085	0.379	0.081	0.082	0.540
F(000)	552	600	584	324	1556
Diffractometer	«Bruker SMART»	«Nonius CAD 4»	«Nonius CAD 4»	«Nonius CAD 4»	«Bruker SMART»
T/K	110(2)	293(2)	293(2)	293(2)	100(2)
θ Scan range	3.49—26.99	2.18—24.99	2.20—24.97	2.34—24.97	1.22—25.50
Ranges of indices of reflections	$-7 \le h \le 7$ $-13 \le k \le 14$ $-23 \le l \le 22$	$-17 \le h \le 17$ $0 \le k \le 14$ $-9 \le l \le 5$	$-9 \le h \le 6$ $0 \le k \le 10$ $-22 \le l \le 22$	$-7 \le h \le 7$ $-10 \le k \le 10$ $-18 \le l \le 18$	$-16 \le h \le 15$ $-19 \le k \le 19$ $-18 \le l \le 20$
Number of measured reflections	5059	3899	4501	5538	22724
Number of independent reflections (R_{int})	1418 (0.0287)	2318 (0.1607)	2486 (0.0363)	2769 (0.0317)	12723 (0.0375)
Number of parameters in refinement	121	172	255	285	857
R_1 ($I \ge 2\sigma(I)$)	0.0357	0.0928	0.0430	0.0371	0.1264
wR_2 (based on all reflections)	0.1033	0.2409	0.1121	0.0971	0.3401
Goodness-of-fit on F^2	1.061	1.063	0.993	0.990	2.008
Residual electron density (max/min)/e Å^{-3}	0.306/−0.135	0.476/−0.449	0.224/−0.183	0.168/−0.125	3.320/−1.550

Table 2. Selected geometric parameters (interplanar angles and bond lengths) in the molecular structures of compounds **6**, **13—15**, and **31**

Compound	Angle/deg			Bond lengths/Å			
	Cen/Het[1]	Cen/Het[2]	Het[1]/Het[2]	C=O	C=C	(O)C—C(=C)	(C=)C—Het
6	5.95(5)	5.95(5)	11.88(5)	1.224(2)	1.345(1)	1.491(1)	1.464(1)
13	21.3(2)	24.9(2)	36.4(2)	1.221(7)	1.337(8)	1.494(8)	1.453(8)
					1.336(8)	1.486(8)	1.444(8)
14	37.5(1)	23.9(1)	22.2(1)	1.219(2)	1.338(3)	1.496(2)	1.465(2)
					1.341(2)	1.505(3)	1.465(3)
15	54.99(5)	39.95(5)	38.10(7)	1.230(2)	1.345(2)	1.505(2)	1.475(2)
					1.354(2)	1.505(2)	1.468(2)
31	46.34(7)	9.8(1)	39.06(8)	1.229(2)	1.337(2)	1.481(2)	1.461(2)
					1.338(2)	1.492(2)	1.451(2)

Note: Cen is the fragment consisting of six atoms and including the carbonyl group and conjugated double bonds and Het is the fragment including the atoms of the heterocyclic substituent.

of one molecule forms two hydrogen bonds with the methylene hydrogen atoms of two translationally related molecules. In the reference molecule, one hydrogen atom of each methylene group is also involved in the formation of analogous bonds with two adjacent molecules, resulting in networks consisting of dimers (Fig. 2). Within these networks, molecules **6** are arranged in a head-to-tail fashion.

When studying the structure of ligand **15**,[20] we found intermolecular C—H...O contacts (2.57(2) and 2.61(2) Å),

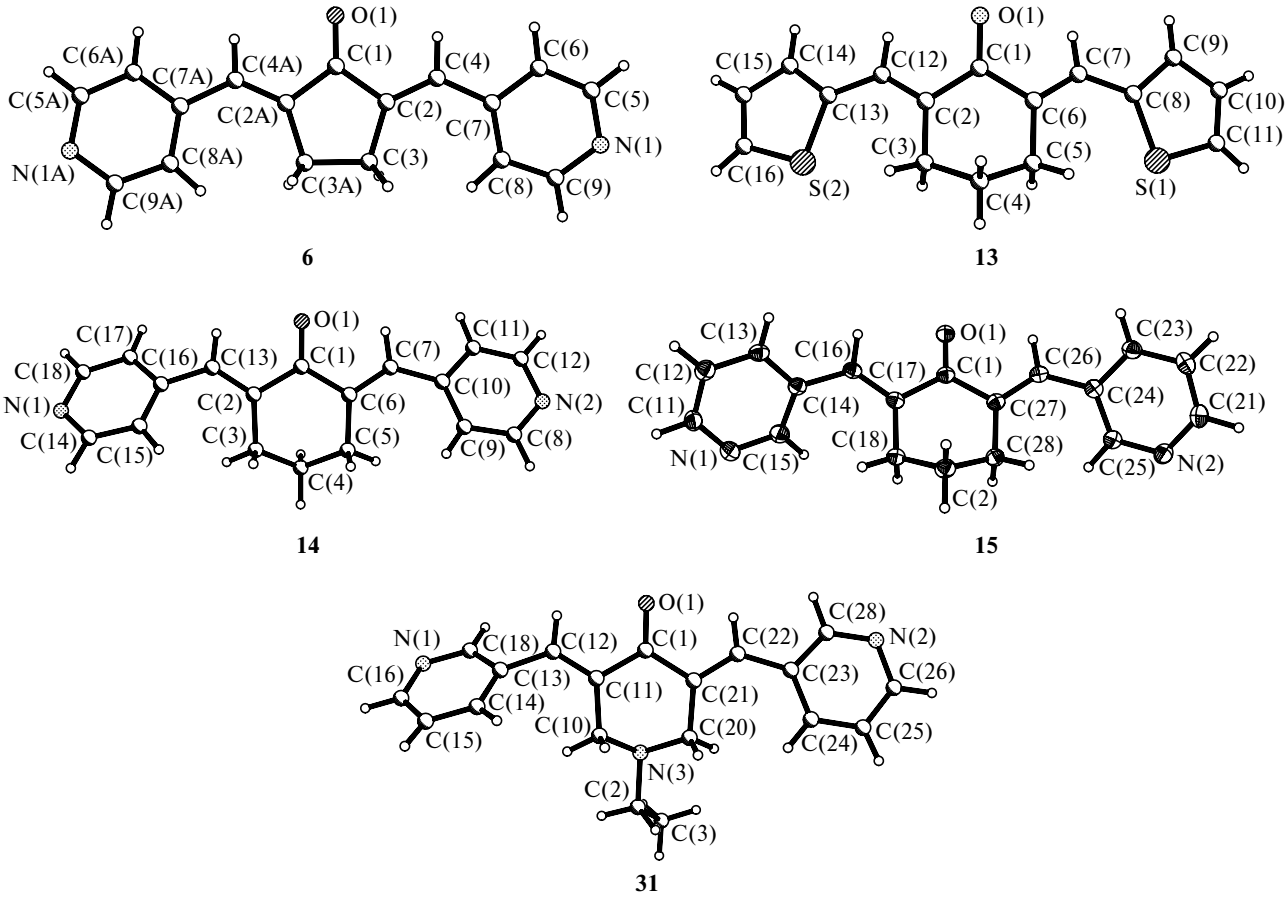


Fig. 1. Molecular structures of compounds **6**, **13—15**, and **31**.

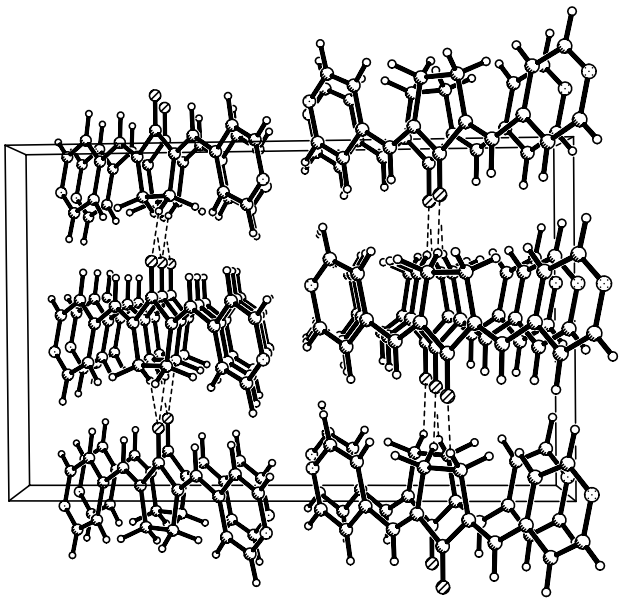


Fig. 2. Molecular packing in the crystal structure of **6**.

which correspond to interactions between the carbonyl oxygen atom and the methylene protons and the α protons of the pyridine rings, respectively. The former interaction results in the formation of chiral head-to-tail dimers, which are packed in stacks along the crystallographic axis *b*. The adjacent stacks are linked to each other by interactions of the latter type. Analogous intermolecular contacts resulting in a similar three-dimensional arrangement of molecules were found in the crystal structure of isomeric compound **14**. The nearest centrosymmetric molecules are linked to each other by two contacts through the O(1) atoms and the axial hydrogen atoms at the C(5) atom (2.63(2) Å). The resulting dimers are packed in stacks along the crystallographic axis *a*.

In the crystal structure of thiophene dienone **13**, the stacking motif is analogous to that found in cyclohexane analogs **14** and **15** (Fig. 3). The molecules in the stack are arranged in a head-to-tail fashion along the crystallographic axis *c*. In **13**, the shortest intermolecular contact is formed between the O(1) atom and the thiophene α proton H(16) from the adjacent stack (2.46 Å).

In the crystal structure of piperidone derivative **31**, there is an interaction between the O(1) atom and the α proton H(28) of the pyridine ring of the centrosymmetric molecule (2.42(2) Å), resulting in the formation of dimers packed in stacks along the crystallographic axis *a* (Fig. 4).

Analysis of the crystal structures of compounds **13**, **6**, **14**, **31**, and **15** demonstrated the absence of π—π-stacking interactions between the heteroaromatic rings.

When attempting to grow single crystals of 2,5-bis[(*E*)-(3-pyridyl)methylidene]cyclopentanone (**7**) in the light from a $MeCN—CCl_4$ mixture during one month, we obtained crystals, which appeared to be (X-ray diffraction data) not the target dienone but its dimerization product at the C=C double bond, *viz.*, dispirododecane **33** (Fig. 5). This [2+2]-cycloaddition could afford four isomers **A—D**. However, we observed the formation of only isomer **B**.

The ^1H NMR spectrum ($CDCl_3$) of dimer **33** shows a characteristic singlet for two equivalent protons of the cyclobutane ring at δ 4.63. The signals of two types of the pyridine rings are also well distinguished. The methylene protons of the cyclopentane rings and the vinyl protons bound to these groups appear as a characteristic ABCDX system (multiplets at δ 2.80, 2.60, 2.30, and 1.50 for the cyclopentane protons) and a broadened triplet at

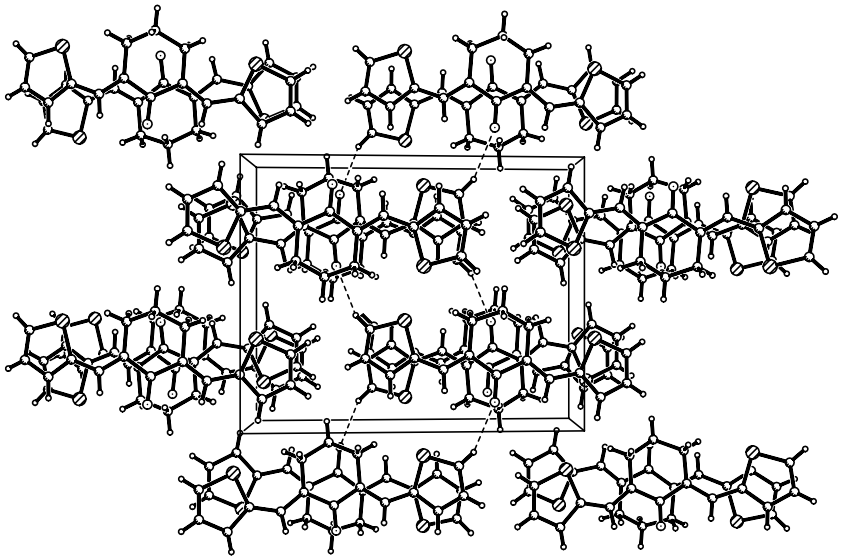


Fig. 3. Molecular packing in the crystal structure of **13**.

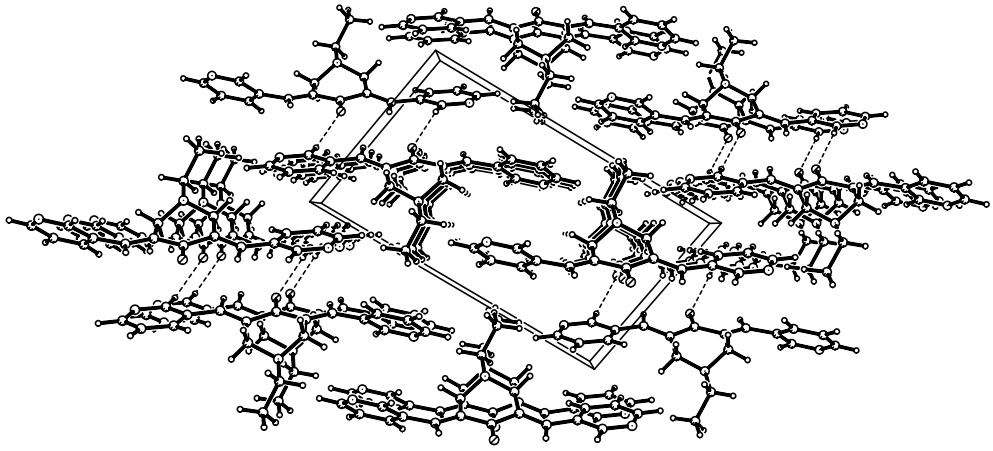
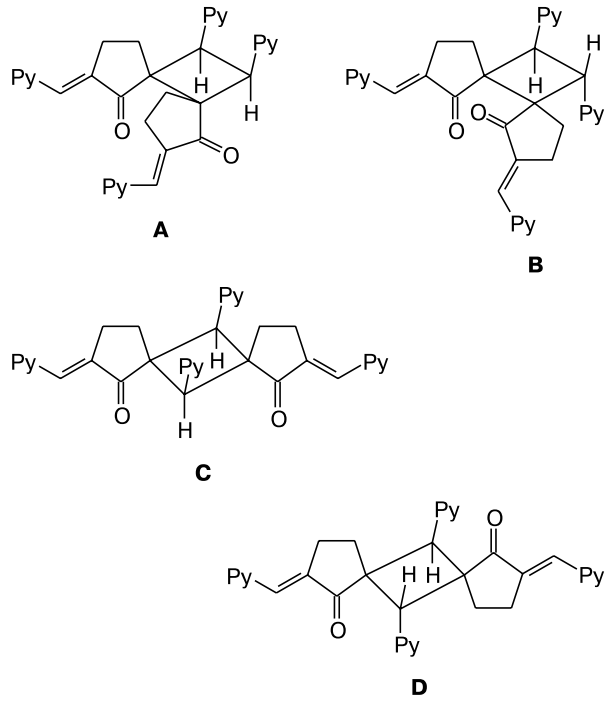


Fig. 4. Molecular packing in the crystal structure of **31**.



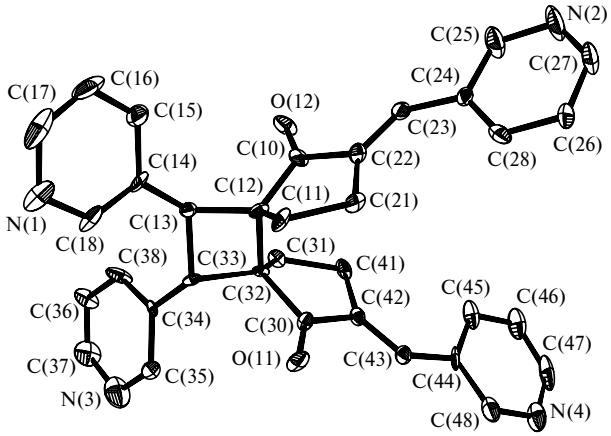


Fig. 5. Molecular structure of compound **33**. Only one of two independent molecules is presented for clarity. The hydrogen atoms and the CCl_4 and water solvent molecules are omitted.

δ 7.52 (CH=). The chemical shifts of these signals, except for the signals for aromatic protons, are virtually equal to those of the phenyl analog, *viz.*, photocyclodimerization product of dienone **1** in a dichloromethane solution.[34]

It was also found[34] that an isomer of type **B** was generated in a mixture of two other photoproducts, whose formation was not observed in our experiments. To the contrary, analysis of the ^{1}H NMR spectra demonstrated that, after heating of dienone **7** in a MeCN—CCl_4 solution in the light, the reaction mixture contained, along with the starting compound **7** and dimer **33**, a product whose spectroscopic characteristics correspond to the *E*,*Z* isomer of compound **7**. This assumption was supported by the presence of the signals for the protons of two nonequivalent CH= groups and two nonequivalent pyridine rings, and an AA´BB´ system of the methylene protons of cyclopentanone. In the reaction mixture, the *E*,*E*-**7** : *E*,*Z*-**7** : **33** ratio was 3.0 : 1.0 : 1.5.

This observation stimulated us to study in detail stability of dienones in solution by NMR spectroscopy. We found that compounds **1, 6, 7, 9, 14, 15, 20,** and **21, 28, 32** in DMSO-d_6 undergo changes associated with the action of light on solutions of the samples. It appeared that the composition and nature of the products depend on the type of the central ring.

For example, when an ampoule with a solution of compound **1** was protected from light, no changes in the ^{1}H NMR spectrum were observed during several days. However, after exposure of the sample to scattered daylight for ~8 h, the spectrum shows additional signals, which can be assigned to the *E*,*Z* isomer.

It should be noted that the ratio of signals of two products remains unchanged in the course of further stor-

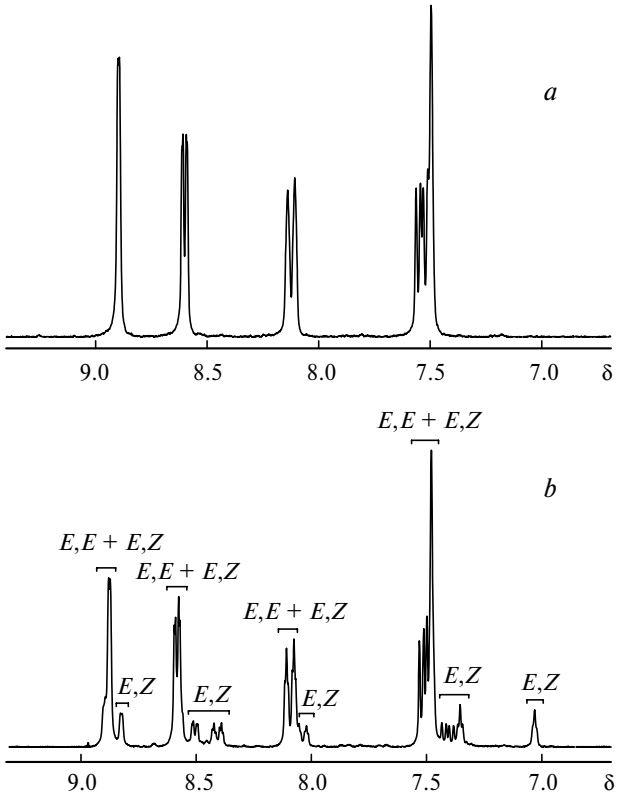


Fig. 6. Fragments of the ^{1}H NMR spectra of compound **7** (DMSO-d_6, aromatic region): storage in the dark for 3 days (*a*) and then in the light for 3 days (*b*). The assignments of the signals of the starting compound (*E*,*E*) and the photoisomerization product (*E*,*Z*) are given.

age in the light. The solvent has no effect on the process, because the same signals are also observed in a solution of **1** in $CDCl_3$. Analogous phenomena were observed for compounds **6** and **7** (Fig. 6).

For cyclohexanone derivatives **9**, **14**, and **15** containing the phenyl or pyridine substituents, processes in solution exposed to light occur in time in a more complex way than those with cyclopentanones. In the first step, products corresponding to *E*,*Z* isomers are rapidly (~1 day) formed, and these products are then slowly transformed into symmetric *Z*,*Z* isomers. The final mixtures contain all possible isomers in a ratio that depends on the nature of the arylidene substituent (Fig. 7, Table 3).

In addition, we demonstrated that 2,7-dibenzylidenecycloheptanone (**34**) and 2,8-dibenzylidenecyclooctanone (**35**) are also photolabile compounds. In the light, both dienones undergo transformations analogous to those found for compound **9** (see Table 3).

Photochemical transformations of pyridine derivatives of piperidones **20**, **21**, **28**, and **32** are complicated by oxidative processes involving the aliphatic nitrogen atom. Nevertheless, the initial step of these transformations also involves *trans*—*cis* photoisomerization.

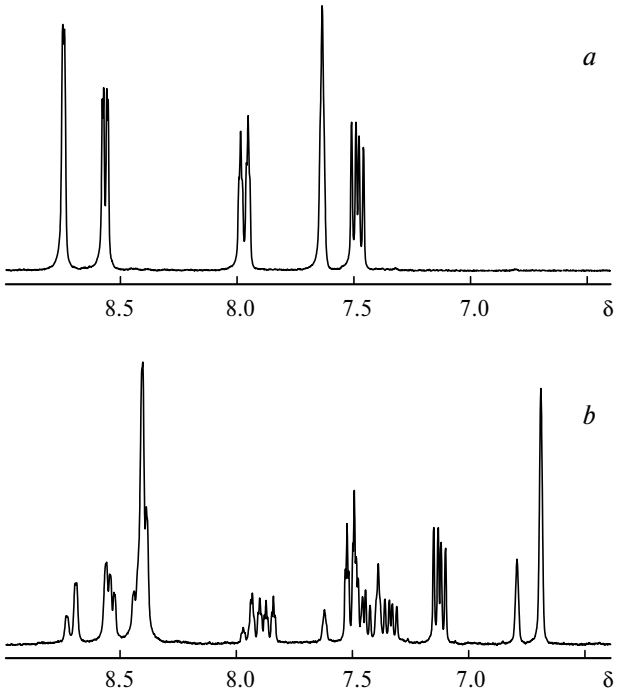


Fig. 7. Fragments of the ^{1}H NMR spectra of compound **15** (DMSO-d_6, aromatic region): storage in the dark for 3 days (*a*) and then in the light for 3 days (*b*).

Table 3. Isomer ratios of dienones after the establishment of the photochemical equilibrium

Ring[a]	Compound	Ratio of stereoisomers					
		E,*E*		*E*,*Z**		*Z*,*Z*	
		Y	δ	Y	δ	Y	δ
C_5	**1**	74	7.46	26	7.34, 6.99	—	—
	6	63	7.42	37	7.28, 7.03	—	—
	7	71	7.50	29	7.37, 7.05	—	—
C_6	**9**	13	7.63	61	—[b], 6.73	26	6.61
	14	12	7.54	45	—[b], 6.78	43	6.68
	15	12	7.62	38	7.40, 6.80	50	6.70
C_7	**34**	—[b]	7.26	1.0[c]	—[b], 6.61	0.38[c]	6.75
C_8	**35**	16	6.96	64	7.56, 6.51	20	6.61

Note. Y (%) is the percentage of the stereoisomer, δ are the chemical shifts of the olefinic protons. For the *E*,*Z* isomer, the first chemical shift belongs to the proton at the double bond in the *E* configuration.

[a] The size of the central ring.

[b] The precise position was not determined because of overlapping of the signals.

[c] Since the precise percentage of the *E*,*E* isomer was not determined because of overlapping of the signals, the ratio of the *E*,*Z* to *Z*,*Z* isomers is given.

To summarize, we demonstrated that the reactions of cyclic ketones with aromatic aldehydes under basic conditions produce cross-conjugated dienones as *E*,*E* iso-

mers. It was found for the first time that this series of compounds can undergo photochemical equilibrium *trans—cis* isomerization in solution under the scattered light. The extent of isomerization is primarily determined by the nature of the central fragment of the dienone molecule. The ketones under study are able to undergo photochemical [2+2]-cycloaddition, as was exemplified by the reaction of 2,5-bis[(*E*)-(3-pyridyl)methylidene]cyclopentanone.

Experimental

The course of the reactions was monitored and the purity of the compounds was checked by thin-layer chromatography (TLC) on a fixed silica gel layer (Silufol plates).

The IR spectra were measured on an UR-20 instrument (in Nujol mulls). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian-VXR-400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C). The chemical shifts are given on the δ scale relative to HMDS as the internal standard (^{1}H) or the signal of the deuterated solvent (^{13}C). Photoisomerization of dienones was studied by NMR spectroscopy on a Bruker Avance 250 instrument (250.130 MHz for ^{1}H NMR spectra and 62.860 MHz for ^{13}C{^{1}H} spectra) in DMSO-d_6.

The solvents were purified and dried according to procedures published in the handbook.[35] The melting points were determined in open capillary tubes on a heating block and are uncorrected. Elemental analysis was carried out on a Carlo-Erba CHN analyzer. 2,7-Dibenzylidenecycloheptanone (**34**) and 2,8-dibenzylidenecyclooctanone (**35**) were prepared according to known procedures.[22,27]

Synthesis of α,β-diarylidene derivatives of cyclic ketones. Method *A* (see Ref. 21). A mixture of ketone (0.01 mol) and aldehyde (0.02 mol) was dissolved in 95% ethanol (15 mL), and a sodium hydroxide solution (0.04 g) in a minimum amount of water was added. The solution was magnetically stirred (TLC monitoring). The precipitate that formed was filtered off and recrystallized from ethanol.

2,5-Bis[(*E*)-phenylmethylidene]cyclopentanone (1) (see Ref. 29), yield 87%, m.p. 196 °C. IR, ν/cm^{-1}: 1690 (C=O), 1610 (C=C). ^{1}H NMR, δ: 3.11 (s, 4 H, C(3)H$_2$, C(4)H$_2$); 7.35—7.50 (m, 10 H, Ph); 7.60 (s, 2 H, CH=).

2,5-Bis[(*E*)-(4-methoxyphenyl)methylidene]cyclopentanone (2) (see Ref. 29), yield 65%, m.p. 198 °C. IR, ν/cm^{-1}: 1700 (C=O), 1610 (C=C). ^{1}H NMR, δ: 2.98 (s, 4 H, C(3)H$_2$, C(4)H$_2$); 3.76 (s, 6 H, OMe); 6.85 (d, 4 H, H(3′), H(5′) (4-OMe-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 7.9 Hz); 7.16 (s, 2 H, CH=); 7.46 (d, 4 H, H(2′), H(6′) (4-OMe-C$_6$H$_4$), $J_{2',6'-3',5''}$ = 7.9 Hz).

2,5-Bis[(*E*)-(4-dimethylaminophenyl)methylidene]cyclopentanone (3), yield 25%, m.p. 298 °C. Found (%): C, 79.50; H, 7.50; N, 7.98. $C_{23}H_{26}N_2O$. Calculated (%): C, 79.73; H, 7.56; N, 8.09. IR, ν/cm^{-1}: 1690 (C=O), 1600 (C=C). ^{1}H NMR, δ: 3.01 (s, 12 H, NMe$_2$); 4.24 (s, 4 H, C(3)H$_2$, C(4)H$_2$); 6.72 (d, 4 H, H(3′), H(5′) (4-NMe)$_2$-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 9.2 Hz); 7.51 (d, 4 H, H(2′), H(6′) ((4-(NMe)$_2$C$_6$H$_4$), $J_{2',6'-3',5''}$ = 9.2 Hz); 7.53 (s, 2 H, CH=).

2,5-Bis[(*E*)-(2-furyl)methylidene]cyclopentanone (4) (see Ref. 36), yield 88%, m.p. 164 °C. Found (%): C, 74.93; H, 4.99. $C_{15}H_{12}O_3$. Calculated (%): C, 74.99; H, 5.03. IR, ν/cm^{-1}: 1690 (C=O), 1615 (C=C). ^{1}H NMR, δ: 3.06 (s, 4 H, C(3)H$_2$, C(4)H$_2$); 6.52 (dd, 2 H, β-H (C$_4$H$_3$O), $J_{\beta-\alpha}$ = 3.5 Hz, $J_{\beta-\beta'}$ = 1.8 Hz); 6.68 (d, 2 H, β′-H (C$_4$H$_3$O), $J_{\beta'-\beta}$ = 1.8 Hz); 7.30 (s, 2 H, CH=); 7.57 (d, 2 H, α-H (C$_4$H$_3$O), $J_{\alpha-\beta}$ = 3.5 Hz). ^{13}C NMR, δ: 25.8 (CH$_2$); 112.6, 115.9, 119.8, 135.9, 145.0, 152.8, 195.3 (C=O).

2,5-Bis[(*E*)-(2-thienyl)methylidene]cyclopentanone (5) (see Ref. 36), yield 96%, m.p. 222 °C. Found (%): C, 66.14; H, 4.44. $C_{15}H_{12}OS_2$. Calculated (%): C, 66.01; H, 4.39. IR, ν/cm^{-1}: 1685 (C=O), 1600 (C=C). ^{1}H NMR, δ: 3.02 (s, 4 H, C(3)H$_2$, C(4)H$_2$); 7.15 (dd, 2 H, β-H (C$_4$H$_3$S), $J_{\beta-\alpha}$ = 4.9 Hz, $J_{\beta-\beta'}$ = 3.6 Hz); 7.38 (d, 2 H, β′-H (C$_4$H$_3$S), $J_{\beta'-\beta}$ = 3.6 Hz); 7.55 (d, 2 H, α-H (C$_4$H$_3$S), $J_{\alpha-\beta}$ = 4.9); 7.78 (s, 2 H, CH=). ^{13}C NMR, δ: 26.0 (CH$_2$); 126.2, 128.1 130.3, 132.6, 135.8, 140.4, 194.4 (C=O).

2,6-Bis[(*E*)-phenylmethylidene]cyclohexanone (9) (see Ref. 29), yield 90%, m.p. 118 °C. IR, ν/cm^{-1}: 1660 (C=O), 1630 (C=C). ^{1}H NMR, δ: 1.90 (m, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.4 Hz); 3.35 (t, 4 H, C(3)H$_2$, C(5)H$_2$, $J_{3,5-4}$ = 5.4 Hz); 7.36—7.56 (m, 10 H, Ph); 7.63 (s, 2 H, CH=).

2,6-Bis[(*E*)-(4-methoxyphenyl)methylidene]cyclohexanone (10) (see Ref. 29), yield 38%, m.p. 142 °C. IR, ν/cm^{-1}: 1665 (C=O), 1590 (C=C). ^{1}H NMR, δ: 1.79 (tm, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.4 Hz); 2.89 (t, 4 H, C(3)H$_2$, C(5)H$_2$, $J_{3,5-4}$ = 5.9 Hz); 3.82 (s, 6 H, OMe); 6.94 (d, 4 H, H(3′), H(5′) (4-OMe-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 9.2 Hz); 7.45 (d, 4 H, H(2′), H(6′) (4-OMe-C$_6$H$_4$), $J_{2'.6'-3'.5'}$ = 9.2 Hz); 7.81 (s, 2 H, CH=). ^{13}C NMR, δ: 22.9 (C(4)H$_2$); 28.5 (C(3)H$_2$, C(5)H$_2$); 55.2 (OMe); 113.8, 128.7, 132.2, 134.3, 136.4, 159.8, 190.1 (C=O).

2,6-Bis[(*E*)-(2-furyl)methylidene]cyclohexanone (11) (see Ref. 36), yield 60%, m.p. 140 °C. Found (%): C, 75.68; H, 5.57. $C_{16}H_{14}O_3$. Calculated (%): C, 75.58; H, 5.55. IR, ν/cm^{-1}: 1660 (C=O), 1590 (C=C). ^{1}H NMR, δ: 1.89 (tm, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.2 Hz); 2.99 (t, 4 H, C(3)H$_2$, C(5)H$_2$, $J_{3,5-4}$ = 5.2 Hz); 3.89 (s, 6 H, OMe); 6.49 (dd, 2 H, β-H (C$_4$H$_3$O), $J_{\beta-\alpha}$ = 3.5 Hz, $J_{\beta-\beta'}$ = 1.4 Hz); 6.64 (d, 2 H, β′-H (C$_4$H$_3$O), $J_{\beta'-\beta}$ = 1.4 Hz); 7.53 (m, 4 H, α-H (C$_4$H$_3$O), CH=)). ^{13}C NMR, δ: 21.7 (C(4)H$_2$); 28.0 (C(3)H$_2$, C(5)H$_2$); 112.3, 116.0, 123.3, 133.0, 144.5, 152.8, 189.0 (C=O).

2,6-Bis[(*E*)-(5-methyl-2-furyl)methylidene]cyclohexanone (12), yield 68%, m.p. 106 °C. Found (%): C, 76.45; H, 6.48. $C_{18}H_{18}O_3$. Calculated (%): C, 76.57; H, 6.43. IR, ν/cm^{-1}: 1660 (C=O), 1600 (C=C). ^{1}H NMR, δ: 1.86 (tm, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.7 Hz); 2.36 (s, 6 H, Me (5-Me-C$_4$H$_2$O)); 2.97 (t, 4 H, C(3)H$_2$, C(5)H$_2$, $J_{3,5-4}$ = 5.7 Hz); 6.11 (d, 2 H, β-H (5-Me-C$_4$H$_2$O), $J_{\beta-\beta'}$ = 3.3 Hz); 6.56 (d, 2 H, β′-H (5-Me-C$_4$H$_2$O), $J_{\beta'-\beta}$ = 3.3 Hz); 7.49 (s, 2 H, CH=).

2,6-Bis[(*E*)-(2-thienyl)methylidene]cyclohexanone (13) (see Ref. 36), yield 86%, m.p. 169 °C. Found (%): C, 66.99; H, 4.89. $C_{16}H_{14}OS_2$. Calculated (%): C, 67.09; H, 4.94. IR, ν/cm^{-1}: 1660 (C=O), 1590 (C=C). ^{1}H NMR, δ: 1.97 (tm, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.71 Hz); 2.95 (t, 4 H, C(3)H$_2$, C(5)H$_2$, $J_{3,5-4}$ = 5.71 Hz); 7.14 (dd, 2 H, β-H (C$_4$H$_3$S), $J_{\beta-\alpha}$ = 5.1 Hz, $J_{\beta-\beta'}$ = 3.7 Hz); 7.37 (d, 2 H, β′-H (C$_4$H$_3$S), $J_{\beta'-\beta}$ = 3.7 Hz); 7.53 (d, 2 H, α-H (C$_4$H$_3$S), $J_{\alpha-\beta}$ = 5.1 Hz); 7.99 (s, 2 H, CH=).

1-Methyl-3,5-bis[(*E*)-phenylmethylidene]-4-piperidone (16) (see Ref. 11), yield 50%, m.p. 118 °C. IR, ν/cm^{-1}: 1680 (C=O), 1630 (C=C). ^{1}H NMR, δ: 2.43 (s, 3 H, Me); 3.74 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.38—7.40 (m, 10 H, Ph); 7.80 (s, 2 H, CH=).

1-Methyl-3,5-bis[(*E*)-(4-methoxyphenyl)methylidene]-4-piperidone (17) (see Ref. 11), yield 44%, m.p. 198 °C. IR, ν/cm^{-1}:

1670 (C=O), 1605 (C=C). ^{1}H NMR, δ: 2.50 (s, 3 H, NMe); 3.79 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 3.90 (s, 6 H, OMe); 6.95 (d, 4 H, H(3′), H(5′) (4-OMe-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 7.2 Hz); 7.40 (d, 4 H, H(2′), H(6′) (4-OMe-C$_6$H$_4$), $J_{2',6'-3',5''}$ = 7.2 Hz); 7.69 (s, 2 H, CH=).

1-Methyl-3,5-bis[(*E*)-(4-dimethylaminophenyl)methylidene]-4-piperidone (18) (see Ref. 11), yield 16%, m.p. 232 °C. IR, ν/cm^{-1}: 1680 (C=O), 1610 (C=C). ^{1}H NMR, δ: 2.49 (s, 3 H, NMe); 3.02 (s, 12 H, NMe$_2$); 3.79 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 6.72 (d, 4 H, H(3′), H(5′) (4-NMe$_2$-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 9.0 Hz); 7.34 (d, 4 H, H(2′), H(6′) (4-NMe$_2$-C$_6$H$_4$), $J_{2',6'-3',5''}$ = 9.0 Hz); 7.76 (s, 2 H, CH=).

1-Methyl-3,5-bis[(*E*)-(2-thienyl)methylidene]-4-piperidone (19) (see Ref. 11), yield 68%, m.p. 118 °C. IR, ν/cm^{-1}: 1665 (C=O), 1610 (C=C). ^{1}H NMR, δ: 2.57 (s, 3 H, Me); 3.78 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.12 (dd, 2 H, β-H (C$_4$H$_3$S), $J_{\beta-\alpha}$ = 4.9 Hz, $J_{\beta-\beta'}$ = 3.5 Hz); 7.30 (d, 2 H, β′-H (C$_4$H$_3$S), $J_{\beta'-\beta}$ = 3.5 Hz); 7.52 (d, 2 H, α-H (C$_4$H$_3$S), $J_{\alpha-\beta}$ = 4.9 Hz); 7.90 (s, 2 H, CH=). ^{13}C NMR, δ: 46.0 (Me); 56.6 (CH$_2$); 127.9, 128.2, 130.4, 133.0, 138.7, 186.1 (C=O).

1-Benzyl-3,5-bis[(*E*)-1-phenylmethylidene]-4-piperidone (22) (see Ref. 37), yield 51%, m.p. 158 °C. IR, ν/cm^{-1}: 1680 (C=O), 1620 (C=C). ^{1}H NMR, δ: 3.69 (s, 2 H, PhCH$_2$); 3.85 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.31—7.38 (m, 15 H, Ph); 7.80 (s, 2 H, CH=).

1-Benzyl-3,5-bis[(*E*)-(4-methoxyphenyl)methylidene]-4-piperidone (23) (see Ref. 37), yield 48%, m.p. 162 °C. IR, ν/cm^{-1}: 1675 (C=O), 1600 (C=C). ^{1}H NMR, δ: 3.70 (s, 2 H, PhCH$_2$); 3.73 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 3.84 (s, 6 H, OMe); 6.88 (d, 4 H, H(3′), H(5′) (4-OMe-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 8.8 Hz); 7.23—7.31 (m, 9 H, H(2′), H(6′) (4-OMe-C$_6$H$_4$), Ph); 7.44 (s, 2 H, CH=).

1-Benzyl-3,5-bis[(*E*)-(4-dimethylaminophenyl)methylidene]-4-piperidone (24) (see Ref. 37), yield 18%, m.p. 208 °C. IR, ν/cm^{-1}: 1660 (C=O), 1600 (C=C). ^{1}H NMR, δ: 2.99 (s, 12 H, NMe$_2$); 3.72 (s, 2 H, PhCH$_2$); 3.87 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 6.72 (d, 4 H, H(3′), H(5′) (4-NMe$_2$-C$_6$H$_4$), $J_{3',5'-2',6'}$ = 5.8 Hz); 7.23—7.29 (m, 9 H, H(2′), H(6′) (4-NMe$_2$-C$_6$H$_4$), Ph); 7.73 (s, 2 H, CH=).

1-Benzyl-3,5-bis[(*E*)-(2-furyl)methylidene]-4-piperidone (25) (see Ref. 37), yield 78%, m.p. 138 °C. IR, ν/cm^{-1}: 1670 (C=O), 1620 (C=C). ^{1}H NMR, δ: 3.74 (s, 2 H, PhCH$_2$); 3.92 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 6.42 (dd, 4 H, β-H (C$_4$H$_3$O), $J_{\beta-\alpha}$ = 5.2 Hz, $J_{\beta-\beta'}$ = 3.3 Hz); 6.53 (d, 2 H, β′-H (C$_4$H$_3$O), $J_{\beta'-\beta}$ = 3.3 Hz); 7.22—7.32 (m, 5 H, Ph); 7.50—7.59 (m, 4 H, α-H (C$_4$H$_3$O), CH=). ^{13}C NMR, δ: 54.1 (C(2)H$_2$, C(6)H$_2$); 61.6 (PhCH$_2$); 112.4, 116.8, 122.0, 127.2, 128.3, 129.1, 130.3, 137.7, 145.0, 152.1, 186.9 (C=O).

1-Benzyl-3,5-bis[(*E*)-(5-methyl-2-furyl)methylidene]-4-piperidone (26) (see Ref. 37), yield 82%, m.p. 168 °C. IR, ν/cm^{-1}: 1665 (C=O), 1610 (C=C). ^{1}H NMR, δ: 2.29 (s, 6 H, Me (MeC$_4$H$_2$O)); 3.77 (s, 2 H, PhCH$_2$); 3.94 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 6.08 (d, 2 H, β-H (5-Me-C$_4$H$_2$O), $J_{\beta-\beta'}$ = 3.4 Hz); 6.50 (d, 2 H, β′-H (5-Me-C$_4$H$_2$O), $J_{\beta'-\beta}$ = 3.4 Hz); 7.25—7.38 (m, 5 H, Ph); 7.44 (s, 2 H, CH=).

1-Benzyl-3,5-bis[(*E*)-(2-thienyl)methylidene]-4-piperidone (27) (see Ref. 37), yield 90%, m.p. 168 °C. IR, ν/cm^{-1}: 1660 (C=O), 1610 (C=C). ^{1}H NMR, δ: 3.80 (s, 2 H, PhCH$_2$); 3.83 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.06 (dd, 2 H, β-H (C$_4$H$_3$S), $J_{\beta-\alpha}$ = 5.2 Hz, $J_{\beta-\beta'}$ = 3.7 Hz); 7.26 (d, 2 H, β′-H (C$_4$H$_3$S), $J_{\beta'-\beta}$ = 3.7 Hz); 7.28—7.37 (m, 5 H, Ph); 7.48 (d, 2 H, α-H (C$_4$H$_3$S), $J_{\alpha-\beta}$ = 5.2 Hz); 7.90 (s, 2 H, CH=). ^{13}C NMR, δ: 54.1 (C(2)H$_2$, C(6)H$_2$); 62.0 (PhCH$_2$); 127.5, 127.8, 128.3, 128.4, 129.2, 130.4, 130.5, 133.1, 137.1, 138.7, 186.6 (C=O).

1-Benzyl-3,5-bis[(*E*)-(4-pyridyl)methylidene]-4-piperidone (28) (see Ref. 37), yield 50%, m.p. 171 °C. IR, ν/cm^{-1}: 1680 (C=O), 1620 (C=C). ^{1}H NMR, δ: 3.72 (s, 2 H, PhCH$_2$); 3.83 (br.s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.17 (d, 4 H, H(2′), H(6′) (C$_5$H$_4$N), $J_{2',6'-3',5'}$ = 5.1 Hz); 7.26 (m, 5 H, Ph); 7.68 (s, 2 H, CH=); 8.64 (br.d, 4 H, H(3′), H(5′) (C$_5$H$_4$N), $J_{3',5'-2',6'}$ = 5.1 Hz).

1-Benzyl-3,5-bis[(*E*)-(3-pyridyl)methylidene]-4-piperidone (29), yield 37%, m.p. 166 °C. Found (%): C, 78.56; H, 5.84; N, 11.38. C$_{24}$H$_{21}$N$_3$O. Calculated (%): C, 78.45; H, 5.76; N, 11.44. IR, ν/cm^{-1}: 1675 (C=O), 1620 (C=C). ^{1}H NMR, δ: 3.71 (s, 2 H, PhCH$_2$); 3.84 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.24 (m, 5 H, Ph); 7.31 (dd, 2 H, H(5′) (C$_5$H$_4$N), $J_{5'-4'}$ = 7.9 Hz, $J_{5'-6'}$ = 4.9 Hz); 7.62 (d, 2 H, H(4′) (C$_5$H$_4$N), $J_{4'-5'}$ = 7.9 Hz); 7.75 (s, 2 H, CH=); 8.56 (d, 2 H, H(6′) (C$_5$H$_4$N), $J_{6'-5'}$ = 4.9 Hz); 8.62 (br.s, 2 H, H(2′) (C$_5$H$_4$N)).

1-Benzyl-3,5-bis[(*E*)-(2-pyridyl)methylidene]-4-piperidone (30) (see Ref. 37), yield 75%, m.p. 125 °C. Found (%): C, 78.13; H, 5.71; N, 11.48. C$_{24}$H$_{21}$N$_3$O. Calculated (%): C, 78.45; H, 5.76; N, 11.44. IR, ν/cm^{-1}: 1680 (C=O), 1620 (C=C). ^{1}H NMR, δ: 3.78 (s, 2 H, PhCH$_2$); 4.24 (s, 4 H, C(2)H$_2$, C(6)H$_2$); 7.13—7.33 (m, 7 H, H(5′) (C$_5$H$_4$N), Ph); 7.39 (d, 2 H, H(3′) (C$_5$H$_4$N), $J_{3'-4'}$ = 7.6 Hz); 7.60 (s, 2 H, CH=); 7.64 (dt, 2 H, H(4′) (C$_5$H$_4$N), $J_{4'-3''}$ = $J_{4'-5'}$ = 7.6 Hz, $J_{4'-6'}$ = 6.0 Hz); 8.61 (dd, 2 H, H(6′) (C$_5$H$_4$N), $J_{6'-4'}$ = 6.0 Hz, $J_{6'-5'}$ = 5.8 Hz).

Method *B* (see Ref. 6). A mixture of aldehyde (0.02 mol) and ketone (0.01 mol) in water (40 mL) was stirred with cooling to 5 °C, and a 10% sodium hydroxide solution (2 mL) was added. The mixture was stirred at 25 °C for 10 h and then neutralized with a dilute hydrochloric acid solution. The precipitate was filtered off and recrystallized from ethanol.

2,5-Bis[(*E*)-(4-pyridyl)methylidene]cyclopentanone (6) (see Ref. 6), yield 50%, m.p. 239 °C, 50%. IR, ν/cm^{-1}: 1670 (C=O), 1630 (C=C). ^{1}H NMR, δ: 3.16 (s, 4 H, CH$_2$); 7.42 (d, 4 H, H(2′), H(6′) (C$_5$H$_4$N), $J_{2',6'-3',5'}$ = 5.9 Hz); 7.49 (s, 2 H, CH=); 8.70 (d, 4 H, H(3′), H(5′) (C$_5$H$_4$N), $J_{3',5'-2',6'}$ = 5.9 Hz). ^{13}C NMR, δ: 26.3 (CH$_2$); 124.1, 131.5, 140.4, 142.4, 150.4, 195.3 (C=O).

2,5-Bis[(*E*)-(3-pyridyl)methylidene]cyclopentanone (7), yield 73%, m.p. 216 °C. Found (%): C, 77.65; H, 5.44; N, 10.56. C$_{17}$H$_{14}$N$_2$O. Calculated (%): C, 77.84; H, 5.38; N, 10.68. IR, ν/cm^{-1}: 1670 (C=O), 1610 (C=C). ^{1}H NMR, δ: 3.16 (s, 4 H, CH$_2$); 7.33 (dd, 2 H, H(5′) (C$_5$H$_4$N), $J_{5'-4'}$ = 7.8 Hz, $J_{5'-6'}$ = 5.0 Hz); 7.57 (s, 2 H, CH=); 7.87 (d, 2 H, H(4′) (C$_5$H$_4$N), $J_{4'-5'}$ = 7.8 Hz); 8.59 (d, 2 H, H(6′) (C$_5$H$_4$N), $J_{6'-5'}$ = 5.0 Hz); 8.85 (br.s, 2 H, H(2′) (C$_5$H$_4$N)).

2,5-Bis[(*E*)-(2-pyridyl)methylidene]cyclopentanone (8) (see Ref. 6), yield 69%, m.p. 195 °C. IR, ν/cm^{-1}: 1690 (C=O), 1610 (C=C). ^{1}H NMR, δ: 3.35 (s, 4 H, CH$_2$); 7.21 (dd, 2 H, H(5′) (C$_5$H$_4$N), $J_{5'-4'}$ = 7.9 Hz, $J_{5'-6'}$ = 4.7 Hz); 7.51 (d, 2 H, H(3′) (C$_5$H$_4$N), $J_{3'-4'}$ = 7.9 Hz); 7.54 (s, 2 H, CH=); 7.72 (dt, 2 H, H(4′) (C$_5$H$_4$N), $J_{4'-3'}$ = $J_{4'-5'}$ = 7.9 Hz, $J_{4'-6'}$ = 1.7 Hz); 8.74 (dd, 2 H, H(6′) (C$_5$H$_4$N), $J_{6'-4'}$ = 1.7 Hz, $J_{6'-5'}$ = 4.7 Hz). ^{13}C NMR, δ: 27.2 (CH$_2$); 122.7, 127.1 131.5, 136.2 141.8, 150.0, 155.1, 198.3 (C=O).

2,6-Bis[(*E*)-(4-pyridyl)methylidene]cyclohexanone (14) (see Ref. 6), yield 98%, m.p. 150 °C. IR, ν/cm^{-1}: 1670 (C=O), 1630 (C=C). ^{1}H NMR, δ: 1.80 (tm, 2 H, C(4)H$_2$, $J_{4-3,5}$ = 5.20 Hz);

2.90 (t, 4 H, C(3)H_2, C(5)H_2, $J_{3,5-4}$ = 5.20 Hz); 7.25 (d, 4 H, H(2′), H(6′) (C_5H_4N), $J_{2',6'-3',5'}$ = 5.8 Hz); 7.64 (s, 2 H, CH=); 8.64 (d, 4 H, H(3′), H(5′) (C_5H_4N), $J_{3',5'-2',6'}$ = 5.8 Hz). ^{13}C NMR, δ: 22.4 (C(4)H_2); 28.2 (C(3)H_2, C(5)H_2); 123.8, 134.2, 143.0, 149.9, 150.1, 189.2 (C=O).

2,6-Bis[(*E*)-(3-pyridyl)methylidene]cyclohexanone (15) (see Ref. 20), yield 72%, m.p. 139 °C. Found (%): C, 78.40; H, 6.00; N, 10.15. $C_{18}H_{16}N_2O$. Calculated (%): C, 78.22; H, 5.85; N, 10.14. IR, ν/cm^{-1}: 1670 (C=O), 1610 (C=C). ^{1}H NMR, δ: 1.83 (m, 2 H, C(4)H_2); 2.92 (m, 4 H, C(3)H_2, C(5)H_2); 7.33 (dd, 2 H, H(5′) (C_5H_4N), $J_{5'-4'}$ = 7.5 Hz, $J_{5'-5'}$ = 5.2 Hz); 7.74 (m, 4 H, H(4′) (C_5H_4N), CH=); 8.55 (d, 2 H, H(6′) (C_5H_4N), $J_{6'-5'}$ = 5.2 Hz); 8.70 (br.s, 2 H, H(2′) (C_5H_4N)). ^{13}C NMR, δ: 22.6 (C(4)H_2); 28.2 (C(3)H_2, C(5)H_2); 123.2, 131.5, 133.5, 136.9, 137.6, 149.2, 151.0, 189.1 (C=O).

1-Methyl-3,5-bis[(*E*)-(4-pyridyl)methylidene]-4-piperidone (20) (see Ref. 11), yield 68%, m.p. 150 °C. Found (%): C, 73.99; H, 6.00; N, 14.35. $C_{18}H_{17}N_3O$. Calculated (%): C, 74.19; H, 5.89; N, 14.35. IR, ν/cm^{-1}: 1680 (C=O), 1625 (C=C). ^{1}H NMR, δ: 2.43 (s, 3 H, Me); 3.71 (s, 4 H, C(2)H_2, C(6)H_2); 7.22 (d, 4 H, H(2′), H(6′) (C_5H_4N), $J_{2',6'-3,5'}$ = 4.6 Hz); 7.65 (s, 2 H, CH=); 8.66 (d, 4 H, H(3′), H(5′) (C_5H_4N), $J_{3',5'-2',6'}$ = 4.6 Hz).

1-Methyl-3,5-bis[(*E*)-(3-pyridyl)methylidene]-4-piperidone (21) (see Ref. 37), yield 72%, m.p. 139 °C. IR, ν/cm^{-1}: 1675 (C=O), 1620 (C=C). ^{1}H NMR, δ: 2.43 (s, 3 H, Me); 3.72 (s, 4 H, C(2)H_2, C(6)H_2); 7.33 (m, 2 H, H(5′) (C_5H_4N)); 7.66 (d, 2 H, H(4′) (C_5H_4N), $J_{4'-5'}$ = 6.7 Hz); 7.72 (s, 2 H, CH=); 8.55 (m, 2 H, H(6′) (C_5H_4N)); 8.62 (br.s, 2 H, H(2′) (C_5H_4N)). ^{13}C NMR, δ: 45.8 (Me); 56.8 (CH_2); 123.4, 130.9, 132.8, 134.6, 137.0, 149.6, 150.9, 185.8 (C=O).

1-Ethyl-2,5-bis[(*E*)-(3-pyridyl)methylidene]-4-piperidone (31), yield 33%, m.p. 219 °C. Found (%): C, 74.68; H, 6.31; N, 13.72. $C_{19}H_{19}N_3O$. Calculated (%): C, 74.73; H, 6.57; N, 13.76. IR, ν/cm^{-1}: 1700 (C=O), 1610 (C=C). ^{1}H NMR, δ: 1.10 (t, 3 H, Me, J = 7.0 Hz); 2.72 (m, 2 H, C$\underline{H}_2$Me); 3.82 (s, 4 H, C(2)H_2, C(6)H_2); 7.36 (m, 2 H, H(5′) (C_5H_4N)); 7.69 (d, 2 H, H(4′) (C_5H_4N), $J_{4'-5'}$ = 7.0 Hz); 7.76 (s, 2 H, CH=); 8.56 (m, 2 H, H(6′) (C_5H_4N)); 8.62 (br.s, 2 H, H(2′) (C_5H_4N)).

1-Isopropyl-2,5-bis[(*E*)-(3-pyridyl)methylidene]-4-piperidone (32), yield 30%, m.p. 173 °C. Found (%): C, 75.26; H, 6.58; N, 13.19. $C_{20}H_{21}N_3O$. Calculated (%): C, 75.21; H, 6.63; N, 13.16. IR, ν/cm^{-1}: 1695 (C=O), 1610 (C=C). ^{1}H NMR, δ: 1.12 (d, 6 H, Me, J = 6.9 Hz); 2.97 (m, 1 H, CH); 3.78 (s, 4 H, C(2)H_2, C(6)H_2); 7.38 (m, 2 H, H(5′) (C_5H_4N)); 7.71 (d, 2 H, H(4′) (C_5H_4N), $J_{4'-5'}$ = 6.9 Hz); 7.73 (s, 2 H, CH=); 8.60 (d, 2 H, H(6′) (C_5H_4N), $J_{5'-6'}$ = 4.6 Hz); 8.68 (br.s, 2 H, H(2′) (C_5H_4N)).

(2*E*,8*E*,5*R,6*R**,11*R**,12*R**)-11,12-Di(3-pyridyl)-2,8-bis[(3-pyridyl)methylidene]dispiro[4.0.4.2]dodecane-1,7-dione (33)**, m.p. 212 °C. Found (%): C, 77.95; H, 5.41; N, 10.57. $C_{20}H_{21}N_3O$. Calculated (%): C, 77.84; H, 5.38; N, 10.68. IR, ν/cm^{-1}: 1710 (C=O), 1630 (C=C). ^{1}H NMR, δ: 1.40—1.50, 2.26—2.40, 2.54—2.62, and 2.75—2.84 (all m, 2 H each, CH_2); 4.63 (s, 2 H, cyclobutane); 7.25—7.30 (m, 4 H, β-Py^1, β-Py^2); 7.52 (br.s, 2 H, CH=); 7.57 (dt, 2 H, γ-Py^2, J_1 = 8.0 Hz, J_2 = 1.8 Hz); 7.69 (dd, 2 H, α-Py^1, J_1 = 4.8 Hz, J_2 = 1.6 Hz); 8.47 (d, 2 H, α′-Py^2, J = 1.6 Hz); 8.50 (dd, 2 H, α-Py^2, J_1 = 4.4 Hz, J_2 = 1.6 Hz); 8.53 (dm,, 2 H, γ-Py^1, J = 8.0 Hz); 8.86 (d, 2 H, α′-Py^1, J = 2.0 Hz).

X-ray diffraction analysis. Experimental intensities of compounds **6**, **13**, **14**, **31**, and **33** were measured on automated Bruker SMART 1000 and Enraf-Nonius CAD 4 diffractometers using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator). Absorption corrections **13**, **14**, and **31** were ignored. Absorption corrections for **6** and **33** were applied based on intensities of equivalent reflections.[38] The structures were solved by direct methods (SHELX-86).[39] All nonhydrogen atoms were refined by the full-matrix least-squares method against F^2 (SHELXL-97)[40] except for the disordered CCl_4 and water solvent molecules in the structure of **33**. All hydrogen atoms in compounds **6**, **13**, **14**, and **31** were located in difference electron density maps and refined isotropically. The hydrogen atoms in the structure of **33** were placed in calculated positions and refined using a riding model. Large final values of the *R* factors and high residual electron densities for the structure of **33** are associated, on the one hand, with a poor quality of the crystals and, on the other hand, with the presence of a large amount of disordered solvent molecules in the structure.

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