STERICALLY CROWDED HETEROCYCLES. VIII. PREPARATIVE PHOTOISOMERIZATION OF SOME IMIDAZO[1,2-*a*]PYRIDINES

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UV-Illumination of (*Z*)-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**1a**) or its 6-methyl and 6-iodo derivatives **1c** and **1g** resulted in minor (*E*)-isomers **2a**, **2c**, and **2g** and prevailing (*E*,*Z*)-mixtures of *N*-(pyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amines **3a**, **3c**, and **3g** while only corresponding furanoic derivatives **3b** and **3d–3f** were obtained from 5-methyl (**1b**), 7-methyl (**1d**), 8-methyl (**1e**), and 5-phenyl (**1f**) derivatives of the (*Z*)-ketone **1a**. VIS-Illumination of (*Z*)-1,3-diphenyl-3-(2-phenylimidazo[1,2-*a*]benzo[*h*]quinolin-3-yl)prop-2-en-1-one (**4**) led to *N*-(benzo[*h*]quinolin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**5**). Photoisomers **2a**, **2c**, **2g**, **3a–3g**, and **5** were isolated and the molecular structure of **3c** was X-ray determined. Mechanism of the photoisomerization is discussed using semiempirical quantum chemical calculations and compared with mass spectra of compounds **1a**, **2a**, **3a**, **1g**, **2g**, and **3g**.

Key words: Photoisomerization; Imidazo[1,2-*a*]pyridines; PM3 Method; X-Ray structure determination.

It is well known that compounds containing (*Z*)-2,4-dien-1-one molecular fragments are thermally and/or photochemically unstable undergoing ring-closure reactions to isomeric 2*H*-pyrans[1–3]. Provided the precursors are available only in unsuitable (*E*)-configuration the heterocyclization can be accomplished only after prior (*E*) → (*Z*) photoisomerization, as in the case of β-ionone[4,5]. In this connection the behaviour of sterically crowded and easily accessible[6,7] (*Z*)-3-imidazo[1,2-*a*]pyridin-3-yl)-1,3-diphenylprop-2-en-1-ones **1** are of interest because of their thermal stability. In addition, the fact that their possible 2*H*-pyran-like isomers do not formally obey the Bredt rule[8] enhanced

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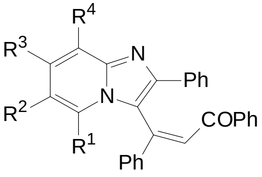
our interest in the UV-photochemistry of **1**-like ketones. In this communication, toluene solutions of compounds **1a–1c** have been UV-illuminated and isolation of the formed reaction products is reported. Mechanistic aspects are also discussed using quantum chemical PM3 and MECI calculations.

We have found that three products are usually present in the illuminated solutions unless the photoprocess is allowed to proceed till the maximum conversion of a given starting compound. It seems that composition of the resulting mixtures depends on the substrate concentration as well as on the reaction time (Table I), but meanwhile the influencies have not been interpreted. The minor components were in all cases (*E*)-stereoisomers **2a–2g** identified by corresponding ^{1}H and ^{13}C NMR spectral patterns, but only derivatives **2a**, **2c**, and **2g** were isolated. On the other hand, the molecular structure assignments of major products by the same means appeared to be not trivial. Hence, X-ray diffraction analysis was performed with iodo derivative formed from (*Z*)-ketone **1g**.



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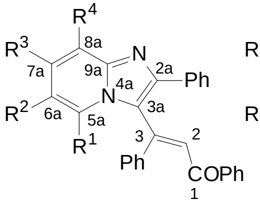

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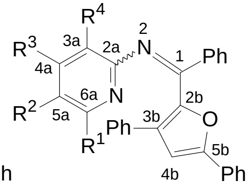


3

1-3	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	H	Me
f	Ph	H	H	H
g	H	I	H	H

The result of the X-ray structure investigation is shown in Fig. 1. It is evident that the crystallized compound is in fact the Schiff base **3g** derived from 2-benzoyl-3,5-diphenylfuran and 2-amino-5-iodopyridine with *Z*-configuration at the C=N bond. It is also evident that a remarkable intramolecular π–π interaction between the phenyl ring at the C3b position and the pyridine ring at the N2 position might be responsible for stabilization of the *Z*-configuration in the investigated solid state of compound **3c**. In addition, this C-T effect may probably result in a restricted rotation around the C1–C2b bond. The shortest contact of 3.051(5) Å belongs to the C2a carbon while the most distant one 3.714(7) Å to the C35 carbon with an overall average about 3.4 Å.

Analogous structures **3a–3f** are considered for the major photoproducts from (*Z*)-ketones **1a–1f** on the basis of NMR spectral similarities to those of the iodo derivative **3g** (see Experimental). However, the spectra exhibit satellite signals indicating (*Z*,*E*) isomerism of the Schiff bases **3a–3g**, at least in solutions. Although our attempts to separate the isomeric couples have been unsuccessful, the *Z*-configuration has been tentatively as-

TABLE I

Yields of products isolated after UV-illumination of (*Z*)-ketones **1a–1g** (22 °C, toluene)

Concentration mmol/l	Reaction time h	(*E*)-Ketone %	(*Z*,*E*)-Imines %	Ratio[a] major/minor
1a (19.9)	6	**2a** (12)	**3a** (65)	4.4
1b (9.6)	7.5	–	**3b** (71)	5.0
1c (20.7)	3	**2c** (13)	**3c** (63)	5.9
1d (2.8)	8	–	**3d** (75)	5.0
1e (20.7)	6	–	**3e** (67)	5.9
1f (11.9)	5	–	**3f** (85)	6.0
1g (19.0)	5	**2g** (10)	**3g** (60)	5.6

[a] According to selected ^{1}H NMR absorptions.

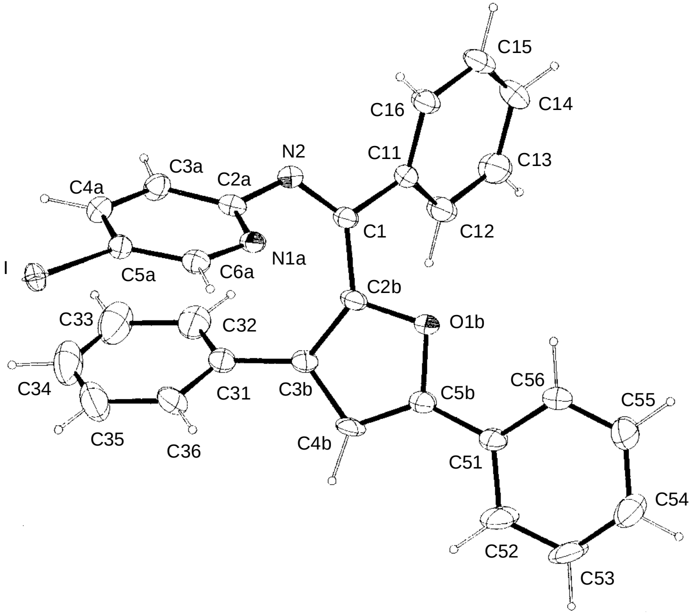


FIG. 1

ORTEP drawing of the molecule **3g** with the atom numbering signed to the prevailing species. It may be noted that the calculated heat of formation ΔH_f for the most stable conformer of the (*Z*)-molecule **3a** is somewhat higher than the ΔH_f value for the (*E*)-configuration (Table II). According to our knowledge, the formation of compounds **3a–3c** seems to be the first example of a dienone → furan photoisomerization[9].

(*Z*)-Ketones **2a**, **2c**, and **2g** were separated from the (*Z*,*E*) mixtures of *N*-(pyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amines **3a**, **3c**, and **3g** by column chromatography and other (*Z*,*E*)-imines **3b**, and **3d–3f** were also obtained in this way.

A possible mechanism of the photoisomerizations **1** → **2** and **1** → **3** may be discussed considering the electronic absorption spectra of the individual components and using the PM3-MECI (refs[10–12]) treatments of the molecules **1a**, **2a**, and **3a**. From the data given in Table II it follows that the calculated Franc–Condon excitation energies $\Delta E(S_0 \rightarrow S_1)$ as well as the corresponding cross-section gaps $\Delta E(S_1 \rightarrow T_1)$ are of very close magni-

TABLE II
PM3-MECI energies of studied molecules (in kcal/mol)

Compound[a]	State	ΔH_f	E_{rel}	$\Delta E(S_0 \rightarrow S_1)$[b]	$\Delta E(S_1 \rightarrow T_1)$[b]
1a (*Z*)	S_0	116.7	1.1	90.4	–35.1
2a (*E*)	S_0	115.6	0.0	89.2	–34.2
3a (*Z*)	S_0	126.3	9.6	97.6	–36.9
3a (*E*)	S_0	126.4	10.8	97.6	–37.1
6a –	T_0	158.2	42.6	–	–

[a] Configuration is given in parentheses; [b] without change in the molecular geometry.

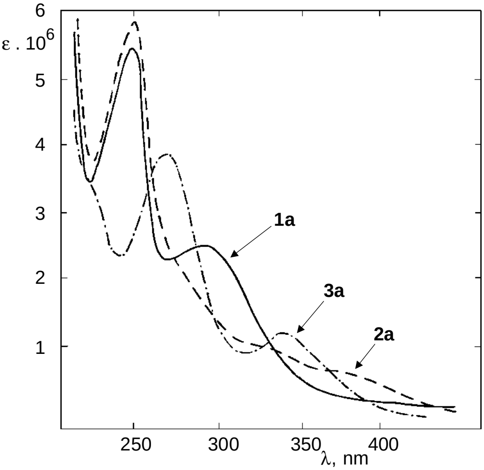
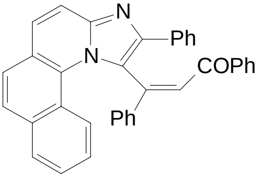


FIG. 2
Comparison of the UV-absorption curves of compounds **1a** (——), **2a** (– – – –), and **3a** (– · – · – ·) in acetonitrile

tudes for all three photoisomers **1a–3a**. Hence, their mutual photochemical interconversions ought to be very probable. In fact, Fig. 2 shows that all absorptions are mutually overlapped enough to enable an effective excitation with UV photons. The long-wave electronic absorption of ketones **1a** and **2a** is apparently of the n_0–π^* nature and therefore a triplet photochemistry of carbonyl substrates[13] involving autosenzibilation effects comes into account. This suggestion is also supported by a lack of observable heavy atom effects on the photochemical transformation of the iodo derivative **3g**.

Further arguments in favour of the interpretation follow from the photoisomerization of (*Z*)-1,3-diphenyl-3-(2-phenylimidazo[1,2-*a*]benzo[*h*]quinolin-3-yl)prop-2-en-1-one (**4**). This (*Z*)-ketone is red, light sensitive and exhibits very broad absorption between 400 and 500 nm. Similarly to several other cases[9], formation of the corresponding (*E*)-isomer is negligible and only furanoic isomers **5** were isolated in 88% yield just after VIS-illumination with an usual tungsten incandescent lamp. On the other hand, formation of the photoisomer **5** was observed to be much more slower with lower conversion during UV-illumination of (*Z*)-ketone **4** under similar conditions as in the cases of compounds **1a–1c**. This may be explained by the fact that the product **5** is yellow, exhibits very low absorption (shoulder) above 400 nm and absorbs visible photons less effectively than the starting red isomer **4**. Hence, the rate of isomerization **4** → **5** with visible photons might be lower in comparison to that for the reverse process. Consequently, UV photons are comparatively absorbed with the both isomers **4** and **5**, rates for the forward and backward processes might be similar and UV-illumination might be less effective.



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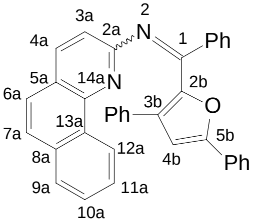

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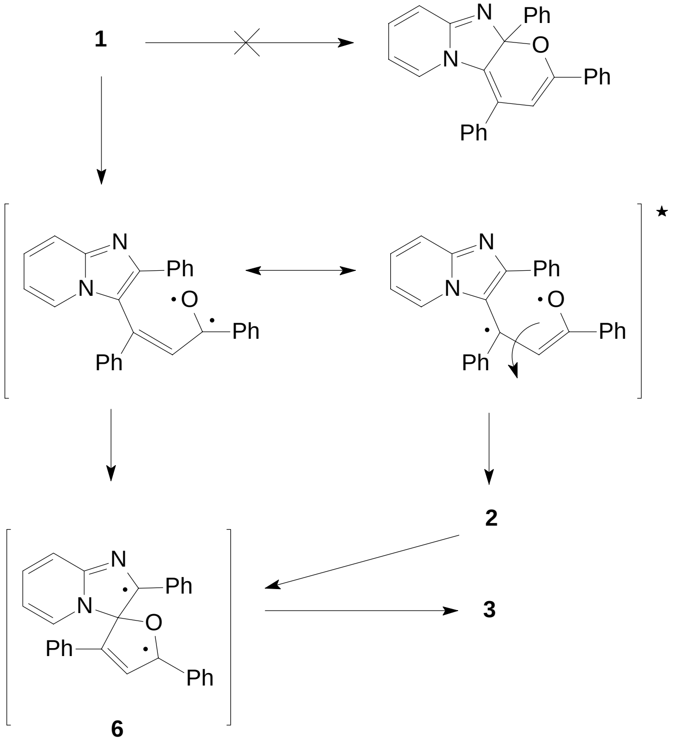
To obtain a deeper insight into the photoreaction mechanism, an expected triplet intermediate has been investigated by means of the MECI procedure[12]. All attempts to optimize the T_1 molecular geometries of isomers **1a**, **2a**, and **3a** have resulted in the same T_0 species represented by the spirocyclic formula **6a** (Fig. 3). In addition, all attempts to transform the PM3 model of triplet intermediate **6a** to its singlet configuration led to one of the ground S_0 state structures **1a**, **2a** or **3a**, respectively. Although the semiempirical PM3-MECI treatment[10–12] can hardly be capable to describe all details and cross-sections of appropriate potential energy hypersurfaces, the computation results implies that the spirocyclizations of types **1** → **6** and **2** → **6** may be really the key steps in the photoconversion of stereoisomeric ketones **1a–1g** and **2a–2g** to furan derivatives **3a–3g** (Scheme 1).

It is of interest that positive-ion electron impact (EI) mass spectra of photoisomers within the triades **1a–2a–3a** and **1g–2g–3g** are almost identical (Table III). Hence, a rapid molecular ion interconversion resembling the photochemically induced mutual isomerizations can be expected. In fact, comparison of the both processes may lead to conclusion that the transformations via radical intermediates (Scheme 1) and via radical cation intermediates (Scheme 2) may be of a similar nature. Consequently, the standard EI spectra exhibit a negligible discrimination for individual photoisomers.

On the other hand, the corresponding FAB mass spectra obtained in 3-nitrobenzyl alcohol matrices after ionization with collision helium pressure exhibit somewhat different fragmentation patterns (Table IV). The most significant difference has been observed for relative intensities of ions *m/z* 181 within the triade **1a–2a–3a** and *m/z* 307 within the triade **1g–2g–3g**. This could be satisfactory explained[9] only in the case of furan derivative **3a**.



SCHEME 1

TABLE III
Principal and daughter ions observed in 70 eV EI spectra of investigated photoisomers **1a–3a** and **1g–3g**

Ion	*m*/*z*	Compound[a]			*m*/*z*	Compound[a]		
		1a	**2a**	**3a**		**1g**	**2g**	**3g**
$M^{+\bullet}$	400	(25)	(27)	(24)	526	(47)	(38)	(37)
$[M - Ph]^+$	323	(12)	(12)	(11)	449	(12)	(12)	(11)
		(25)[b]	(41)[b]	(23)[b]		(30)[b]	(30)[b]	(33)[b]
$[M - PhCO]^+$	295	(100)	(100)	(100)	421	(100)	(100)	(100)
		(100)[b]	(100)[b]	(100)[b]		(100)[b]	(100)[b]	(100)[b]
$[M - Ph - I]^+$	–	–	–	–	322	(7)	(6)	(7)
	–	–	–	–		(5)[b]	(5)[b]	(5)[b]
$[M - PhCO - HI]^+$	–	–	–	–	293	(32)	(29)	(30)
	–	–	–	–		(5)[b]	(5)[b]	(5)[b]
?	–	–	–	–	292	(15)	(13)	(12)
$[M - Ph - PhCO]^{+\bullet}$	218	(5)	(5)	(4)	–	–	–	–
$C_5H_3NI^+$	–	–	–	–	204	(6)	(4)	(9)
?	200	(3)	(3)	(3)	–	–	–	–
?	191	(5)	(3)	(6)	191	(4)	(3)	(7)
$PhCO^+$	105	(10)	(10)	(10)	105	(16)	(15)	(17)
$C_5H_4N^+$	78	(11)	(9)	(13)	78	(2)	(1)	(5)
$C_6H_5^+$	77	(11)	(12)	(8)	77	(16)	(12)	(19)
$C_4H_3^+$	51	(5)	(5)	(4)	51	(4)	(2)	(4)

[a] Relative intensities in % are given in parentheses; [b] daughter ions of ions $M^{+\bullet}$ observed in corresponding CAD B/E mass spectra.

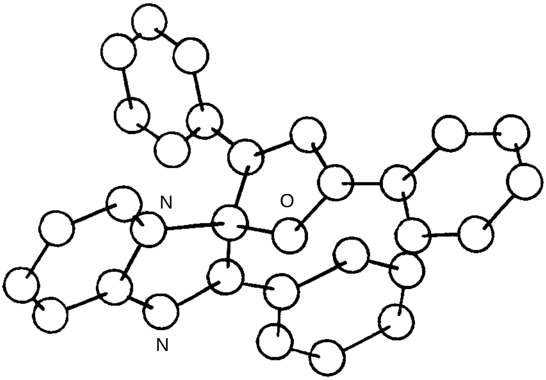
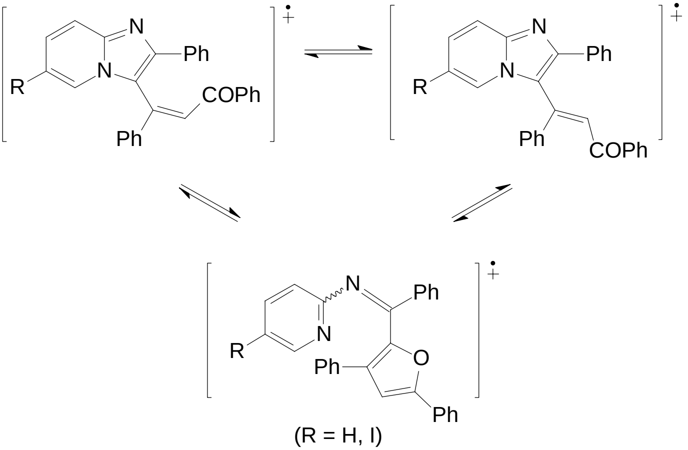


FIG. 3
Molecular shape of spirocyclic intermediate **6a** obtained by the PM3-MECI optimization

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block, the NMR spectra (δ, ppm; *J*, Hz; $CDCl_3$) were taken on a Gemini 300 HC instrument. The working frequency was 300 MHz for ^{1}H and 75 MHz for ^{13}C. The IR spectra ($\tilde{\nu}$, cm^{-1}, $CHCl_3$) were measured on a FTIR spectrometer Nicolet 704.

All EI mass spectra were recorded on a double-sector instrument (Finnigan MAT 90, Bremen, Germany) of BE geometry (ionizing energy 70 eV, source temperature 200 °C, emission current 0.5 mA, accelerating voltage 5 kV, direct inlet, DIP temperature varied between 150–190 °C, samples dosed in microgram amounts for evaporation).



SCHEME 2

TABLE IV
Daughter ions of protonated molecules observed in CAD B/E mass spectra of investigated photoisomers **1a–3a** and **1g–3g**

Ion	*m*/*z*	Compound[a]			*m*/*z*	Compound[a]		
		1a	**2a**	**3a**		**1g**	**2g**	**3g**
$[MH - 30]^+$	371	(8)	(7)	(1)	497	(3)	(5)	(1)
$[M - Ph]^+$	323	(18)	(20)	(22)	449	(30)	(45)	(45)
$[M - PhCO]^+$	295	(100)	(100)	(100)	421	(100)	(100)	(100)
$[MH - C_{12}H_8N_2X]^+$	219	(6)	(5)	(0)	345	(7)	(3)	(1)
$[C_{12}H_8N_2X]^+$	181	(8)	(6)	(50)	307	(13)	(17)	(60)

[a] Relative intensities in % are given in parentheses.

All FAB mass spectra were recorded on the same instrument. The standard saddle field FAB gun (Ion Tech Ltd., Teddington, England) was operated at 2 mA current and 6 kV energy, using xenon as a bombarding gas (10^{-3} Pa). 3-Nitrobenzyl alcohol (Aldrich Chemie, Steinheim, Germany) was used as a matrix. The liquid nitrogen baffle was mounted on the ion source to cool the FAB volume during the operation. The calibration was performed with Ultramark 1600F (PCR Inc., Gainesville, U.S.A.) as a standard.

The products of collisionally activated decompositions in the first field-free region of the instrument were analyzed by daughter ion linked scan (B/E constant) using the manufacturer's software. The collision gas (He) pressure was adjusted for 50% attenuation of the primary ion beam, with collision cell voltage maintained at the ground potential. The mass range was scanned at a rate of 20 s/100 amu and the conventional resolution of the instrument was adjusted to 2 000 (10% valley definition). For the reproducibility confirmation of reported fragmentation patterns also the products of unimolecular decomposition of protonated molecules (in the second field-free region) were detected by MIKES experiments.

High-resolution measurements were carried out by the peak-matching method using a rotatable FAB target with sample deposited on one side and Ultramark 1600F as a standard on the other side. The instrument was tuned to a resolution of 8 000 (10% valley definition). The results are given in Table V.

Preparation of the starting (*Z*)-ketones **1a–1g** was described earlier[7,14,15], but in the case of (*Z*)-3-(5-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)-1,3-diphenyl-prop-2-en-1-one (**1b**), m.p. 191–192 °C, some data[7] are corrected. IR spectrum: 1 659 (C=C–C=O). ^{1}H NMR spectrum: 2.453 s, 3 H (Me); 6.437 dmt, 1 H, *J* = 6.8 (H-6a); 7.068 dd, 1 H, *J* = 6.8 and 9.0 (H-7a); 7.12 mt, 3 H (*m*,*p*-Ph2a);

TABLE V
Results of high resolution mass measurements for compounds **1a–3a** and **1g–3g**

Isomer	Method	Ion	Formula	Mass, *m*/*z*	
				calculated	measured
1a	EI	$M^{+\bullet}$	$C_{28}H_{20}N_2O$	400.1576	400.1585
1a	EI	$[M - Ph]^+$	$C_{22}H_{15}N_2O$	323.1184	323.1183
1a	EI	$[M - PhCO]^+$	$C_{21}H_{15}N_2$	295.1235	295.1239
1a	EI	$[M - Ph - PhCO]^+$	$C_{15}H_{10}N_2$	218.0844	218.0850
1a	EI	Py^+	C_5H_4N	78.0344	78.0340
1a	FAB	$[MH - C_{12}H_9N_2]^+$	$C_{15}H_{11}N_2$	219.0922	219.0950
1g	EI	$M^{+\bullet}$	$C_{28}H_{19}IN_2O$	526.0541	526.0640
2a	EI	$M^{+\bullet}$	$C_{28}H_{20}N_2O$	400.1576	400.1590
2g	EI	$M^{+\bullet}$	$C_{28}H_{19}IN_2O$	526.0541	526.0600
3a	EI	$M^{+\bullet}$	$C_{28}H_{20}N_2O$	400.1576	400.1580
3a	FAB	$[MH - C_{15}H_{11}N_2]^+$	$C_{12}H_9N_2$	181.0766	181.0759
3g	EI	$M^{+\bullet}$	$C_{28}H_{19}IN_2O$	526.0541	526.0630

7.187 dd, 2 H, *J* = 7.7 and 7.7 (*m*-Ph1); 7.37 mt, 3 H (*m*,*p*-Ph3); 7.470 dmt, 3 H, *J* = 7.4 (*o*-Ph3); 7.520 dmt, 2 H, *J* = 7.7 (*o*-Ph1); 7.52 dmt, 1 H, *J* = 9.0 (H-8a); 7.594 dmt, 2 H, *J* = 8.0 (*o*-Ph2a); 7.630 s, 1 H (H-2). ^{13}C NMR spectrum: 19.94 (Me), 113.19 CH (C-6a), 115.21 CH (C-8a), 117.71 C (C-3a), 125.87 CH (C-7a), 127.17 CH (*p*-Ph2a), 127.23 CH (*o*-Ph3), 127.68 CH (*o*-Ph1), 127.80 CH (*m*-Ph2a), 127.85 CH (*o*-Ph2a), 127.91 CH (*m*-Ph1), 129.15 CH (*m*-Ph3), 129.22 (C-2), 129.86 CH (*p*-Ph3), 132.26 CH (*p*-Ph1), 133.88 C (*i*-Ph2a), 136.44 C (C-5a), 137.30 (*i*-Ph1), 139.90 C (*i*-Ph3), 143.37 C (C-3), 144.15 C (C-2a), 146.70 C (C-9a), 191.28 C (C-1).

Photoisomerization of Compounds **1a–1g**

A solution of a given (*Z*)-ketone **1** (0.4–3.0 g) in toluene (250–350 ml) was irradiated in an immersion-cell reactor with a water-cooled quartz finger containing a medium pressure UV lamp (RVK 125 W, Tesla) at 22 °C. The reaction mixture was stirred by bubbling through dry nitrogen. The reaction was monitored by HPLC and finished till an equilibrium composition was stabilized (max. 8 h, see Table I). The solvent was distilled off at diminished pressure, the residue was chromatographed on a silica gel

TABLE VI
Data collection and structure refinement parameters for compound **3g**

Crystal dimensions	0.48 × 0.10 × 0.18 mm
Diffractomer and radiation used	Enraf–Nonius CAD4, CuKα_1, λ = 1.54056 Å
Scan technique	$\omega/2\theta$
Temperature	293 K
No. and θ range of reflections for lattice parameter refinement	20; 35–40°
Range of *h*, *k*, and *l*	$-12 \rightarrow 12$, $-22 \rightarrow 22$, $0 \rightarrow 10$
Standard reflections monitored in interval; intensity fluctuation	60 min; –0.3%
Total number of reflections measured; 2θ range	5 907; 0–110°
No. of unique reflections	2 934
No. of observed reflections	2 828
Criterion for observed reflections	$I \geq 1.96\sigma(I)$
Function minimized	$\sum w\,(\lvert F_o \rvert - \lvert F_c \rvert)^2$
Weighting scheme	Chebychev polynomial (ref.[17])
Parameters refined	289
Value of *R*, *wR* and *S*	0.0448, 0.0517, 1.154
Ratio of max. least-squares shift to e.s.d. in the last cycle	0.003
Max. and min. heights in final map	0.852, –0.975 e Å^{-3}
Source of atomic scattering factors	International Tables for X-Ray Crystallography (ref.[18])
Programs used	CRYSTALS (ref.[19]), PARST91 (ref.[20]), SIR92 (ref.[21])

TABLE VII
Final atomic parameters for compound **3g** with e.s.d's in parentheses. The isotropic equivalent parameter is defined as $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$

Atom	x	y	z	U_{eq}, Å^2
I	0.24807(3)	0.26217(2)	–0.66683(4)	0.0448(2)
O1b	0.6914(3)	0.1007(2)	0.0042(3)	0.0323(12)
N2	0.6160(4)	0.0605(2)	–0.3456(4)	0.0338(14)
C1	0.6547(4)	0.0516(2)	–0.2153(5)	0.0310(16)
N1a	0.5448(3)	0.1650(2)	–0.3692(4)	0.0334(15)
C11	0.7577(4)	0.0069(3)	–0.1629(5)	0.0334(18)
C51	0.7049(4)	0.1570(3)	0.2103(5)	0.0371(19)
C6a	0.4643(5)	0.2079(3)	–0.4421(5)	0.0369(19)
C5a	0.3675(4)	0.1929(2)	–0.5556(5)	0.0342(20)
C2b	0.6049(4)	0.0810(2)	–0.1139(5)	0.0325(20)
C4a	0.3498(5)	0.1311(3)	–0.5980(5)	0.0399(18)
C5b	0.6299(4)	0.1302(3)	0.0822(5)	0.0365(20)
C2a	0.5273(4)	0.1052(2)	–0.4116(5)	0.0333(19)
C3a	0.4326(5)	0.0868(2)	–0.5259(5)	0.0381(18)
C3b	0.4900(4)	0.0955(2)	–0.1098(5)	0.0312(18)
C4b	0.5085(4)	0.1280(3)	0.0181(5)	0.0327(21)
C31	0.3717(4)	0.0818)3)	–0.2147(5)	0.0377(20)
C13	0.8585(6)	–0.0754(3)	–0.0098(6)	0.0556(24)
C16	0.8464(5)	0.0020(3)	–0.2286(5)	0.0414(20)
C12	0.7650(5)	–0.0323(3)	–0.0524(6)	0.0440(21)
C56	0.8303(5)	0.1629(3)	0.2405(6)	0.0474(21)
C32	0.3453(6)	0.0220(3)	–0.2685(6)	0.0547(27)
C36	0.2850(5)	0.1282(4)	–0.2545(7)	0.0522(25)
C52	0.6544(6)	0.1804(4)	0.3065(7)	0.0569(33)
C14	0.9469(5)	–0.0790(3)	–0.0752(7)	0.0538(26)
C34	0.1485(7)	0.0567(6)	–0.4042(8)	0.0724(40)
C15	0.9402(5)	–0.0412(3)	–0.1846(6)	0.0491(25)
C54	0.8510(6)	0.2094(4)	0.4564(6)	0.0614(30)
C33	0.2313(7)	0.0091(5)	–0.3663(7)	0.0724(35)
C55	0.9030(6)	0.1878(4)	0.3621(6)	0.0599(27)
C53	0.7285(7)	0.2058(5)	0.4296(7)	0.0610(39)
C35	0.1726(6)	0.1154(5)	–0.3506(8)	0.0707(36)

column (150 g) in toluene–chloroform–ether mixture and individual substances were crystallized from suitable solvents.

(E)-3-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2a**): yellow crystals, m.p. 154–156 °C (heptane–toluene). For $C_{28}H_{20}N_2O$ (400.5) calculated: 83.98% C, 5.03% H, 6.99% N; found: 84.26% C, 5.00% H, 6.88% N. IR spectrum: 1 635 and 1 657 (C=C–C=O). ^{1}H NMR spectrum: 6.63 ddd, 1 H, *J* = 6.9, 7.0 and ≈1.1 (H-6a); 6.96 s, 1 H (H-2); 7.16–7.45 m, 11 H; 7.45–7.52 m, 1 H; 7.55 d, 1 H, *J* = 7.0 (H-5a); 7.69 d, 1 H, *J* = 9.2 (H-8a); 7.75–7.81 m, 2 H (*o*-Ph1 or *o*-Ph2a); 7.92–7.99 m, 2 H (*o*-Ph1 or *o*-Ph2a). ^{13}C NMR spectrum: 113.34 CH (C-6a), 118.46 CH (C-8a), 121.94 C (C-2a or C-3a), 125.34 CH, 126.09 CH, 128.80 CH, 129.12 CH, 129.29 CH, 129.47 CH, 129.48 CH, 129.53 CH, 129.97 CH, 130.33 CH, 130.97 CH, 133.68 CH, 134.76 C, 136.69 C, 138.30 C, 141.67 C (C-10 or C-3), 146.49 C (C-2a or C-3a), 147.04 C (C-9a), 192.90 C (C-1).

(E)-(6-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl-1,3-diphenylprop-2-en-1-one (**2c**): yellow crystals, m.p. 172–174 °C (diethyl ether). For $C_{29}H_{22}N_2O$ (414.5) calculated: 84.03% C, 5.35% H, 6.76% N; found: 83.85% C, 5.48% H, 6.60% N. IR spectrum: 1 656 (C=C–C=). ^{1}H NMR spectrum: 2.13 s, 3 H (Me-6); 6.96 s, 1 H (H-2); 7.05 dd, 1 H, *J* = 9.2 and < 1.2 (H-7a); 7.21–7.43 m, 11 H; 7.43–7.51 m, 1 H; 7.59 d, 1 H, *J* = 9.2 (H-8a); 7.79 dd, 2 H, *J* = 8.4 and < 1.2 (*o*-Ph1 or *o*-Ph2a); 7.93 dd, 2 H, *J* =

TABLE VIII
Selected bond distances (Å) and angles (°) with e.s.d's in parentheses for compound **3g**

Atoms	Distances	Atoms	Angles
I–C5a	2.096(5)	C2b–O1b–C5b	106.7(3)
O1b–C2b	1.371(6)	C1–N2–C2a	124.5(4)
O1b–C5b	1.370(6)	N2–C1–C11	116.9(4)
N2–C1	1.280(6)	C11–C1–C2b	117.4(4)
N2–C2a	1.407(6)	N2–C1–C2b	125.6(4)
C1–C11	1.485(7)	C6a–N1a–C2a	117.2(4)
C1–C2b	1.469(7)	C1–C11–C16	119.8(4)
N1a–C6a	1.348(6)	C1–C11–C12	121.4(4)
N1a–C2a	1.341(7)	C5b–C51–C56	121.8(5)
C51–C5b	1.443(7)	N1a–C6a–C5a	123.2(5)
C6a–C5a	1.374(7)	O1b–C2b–C1	114.6(4)
C5a–C4a	1.381(7)	O1b–C2b–C3b	110.3(4)
C2b–C3b	1.371(7)	C1–C2b–C3b	135.1(5)
C4a–C3a	1.382(7)	O1b–C5b–C51	115.9(4)
C5b–C4b	1.347(7)	O1b–C5b–C4b	110.3(4)
C2a–C3a	1.384(7)	C51–C5b–C4b	133.8(5)
C3b–C4b	1.435(7)	C2b–C3b–C4b	105.3(4)
C3b–C31	1.478(7)	C5b–C4b–C3b	107.3(4)

8.0 and < 1.2 (*o*-Ph2a or *o*-Ph1). ^{13}C NMR spectrum: 18.94 CH_3 (Me-6), 117.62 CH (C-8a), 121.60 C (C-2a or C-3a), 122.92 C (C-6a), 122.95 CH, 128.57 CH, 129.03 CH, 129.13 CH, 129.16 CH, 129.30 CH, 129.37 CH, 129.92 CH, 130.17 CH, 130.65 CH, 133.58 CH, 134.79 C, 136.72 C, 138.25 C, 141.88 C (C-3), 145.44 C (C-2a or C-3a), 146.64 C (C-9a), 192.87 C (C-1). One CH signal is overlapped.

(E)-3-(6-Iodo-2-phenylimidazo[1,2-a]pyridin-3-yl)-1,3-diphenylprop-2-en-1-one (**2g**): yellow crystals, m.p. 180–182 °C (heptane–toluene). For $C_{28}H_{19}IN_2O$ (526.4): 63.89% C, 3.64% H, 5.32% N, 24.11% I; found: 63.69% C, 3.78% H, 5.11% N, 23.96% I. IR spectrum: 1 659 (C=C–C=O). ^{1}H NMR spectrum: 6.97 s, 1 H (H-2); 7.24–7.54 m, 15 H (Ph); 7.76–7.83 m, 3 H (H-5a and *o*-Ph1 or *o*-Ph2a); 7.90–7.97 m, 2 H (*o*-Ph2a or *o*-Ph1). ^{13}C NMR spectrum: 76.26 C (C-6a), 119.34 CH (C-8a), 121.73 C (C-2a or C-3a), 129.05 CH, 129.16 CH, 129.33 CH, 129.41 CH, 129.46 CH, 129.59 CH, 129.80 CH, 130.33 CH, 130.53 CH, 131.49 CH, 133.83 CH, 134.02 CH, 134.07 C, 136.18 C, 138.07 C, 140.94 C (C-3), 144.82 C (C-2a or C-3a), 146.90 C (C-9a), 192.78 C (C-1).

N-(Pyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylideneamine (**3a**): yellow crystals, m.p. 123–125 °C (heptane–toluene). For $C_{28}H_{20}N_2O$ (400.5) calculated: 83.98% C, 5.03% H, 6.99% N; found: 84.12% C, 5.14% H, 6.90% N. IR spectrum: 1 607 (C=N). ^{1}H NMR spectrum: 6.72 d, 1 H, *J* = 7.9 (H-3a); 6.78 s, 1 H (H-4b); 6.86 dd, 1 H, *J* = 6.9 and 5.2 (H-5a); 7.15 s, 5 H (Ph); 7.24–7.49 m, 9 H (Ph); 7.84 d, 2 H, *J* = 8.0 (*o*-Ph); 8.24 dd, 1 H, *J* = 5.0 and ≈1.1 (H-6a). ^{13}C NMR spectrum: 107.70 CH, 116.47 CH, 119.51 CH, 124.90 CH, 128.08 CH, 128.75 CH, 128.81 CH, 128.91 CH, 129.29 CH, 130.28 CH, 130.33 C, 131.83 CH, 132.46 C, 132.67 C, 137.38 CH, 138.13 C, 143.35 C (C-5b), 148.93 CH (C-6a), 155.43 C (C-2b), 160.49 C (C-1), 163.99 C (C-2a). One CH signal is overlapped.

N-(6-Methylpyridin-2-yl-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3b**): yellow solid, m.p. 50–55 °C (dried in vacuo only). For $C_{29}H_{22}N_2O$ (414.5) calculated: 84.03% C, 5.35% H, 6.76% N; found: 84.01% C, 5.39% H, 6.70% N. IR spectrum: ≈1 610 (C=N), 1 588 and 1 584 (furan and pyridine rings). ^{1}H NMR spectrum: 2.35 s, 3 H (CH_3-6a); 6.44 d, 1 H, *J* = 7.8 (H-3a); 6.70 d, 1 H, *J* = 7.7 (H-5a); 6.78 s, 1 H (H-4b); 7.16 s, 5 H (Ph); 7.20–7.45 m, 7 H (Ph); 7.51 d, 2 H, *J* = 7.7 (*o*-Ph); 7.92 d, 2 H, *J* = 8.1 (*o*-Ph). Satellites: 2.47 s (Me); 6.26 d, *J* = 7.7; 6.86–7.20 m; 7.83 d, *J* = 7.3. ^{13}C NMR spectrum: 24.75 CH_3 (Me-6a), 107.24 CH, 112.11 CH, 118.71 CH, 124.68 CH, 127.89 CH, 128.43 CH, 128.55 CH, 129.14 CH, 130.05 CH, 130.21 C, 131.70 CH, 132.30 C, 137.61 CH, 137.88 C, 143.17 C, 155.02 C (C-2b), 157.64 C (C-6a), 160.23 C (C-1), 163.24 C (C-2a). Two signals (C and CH) are overlapped.

N-(5-Methylpyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3c**): yellow solid, m.p. 101–103 °C (dried in vacuo only). For $C_{29}H_{22}N_2O$ (414.5) calculated: 84.03% C, 5.35% H, 6.76% N; found: 83.92% C, 5.41% H, 6.62% N. IR spectrum: ≈1 600 (sh) (C=N), 1 593 (furan and pyridine rings). ^{1}H NMR spectrum: 2.21 s, 3 H (CH_3-5a); 6.63 d, 1 H, *J* = 7.8 (H-3a); 6.78 s, 1 H (H-4b); 7.15 s, 5 H (Ph); 7.21–7.50 m, 9 H (Ph); 7.85 d, 2 H, *J* = 7.1 (*o*-Ph); 8.06 s, 1 H (H-6a). ^{13}C NMR spectrum: 18.38 CH_3 (Me-5a), 107.61 CH, 115.91 CH, 124.86 CH, 127.96 CH, 128.67 CH, 128.80 CH, 129.23 CH, 130.17 CH, 130.37 C, 131.66 CH, 132.00 C, 132.66 C, 138.03 CH, 138.31 C, 143.40 C (C-5b), 148.76 CH (C-6a), 155.26 C (C-2b), 160.36 C (C-1), 161.61 C (C-2a). One C and two CH signals are overlapped.

N-(4-Methylpyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3d**): yellow solid, m.p. 55–60 °C (dried in vacuo only). For $C_{29}H_{22}N_2O$ (414.5) calculated: 84.03% C, 5.35% H, 6.76% N; found: 83.97% C, 5.3% H, 6.72% N. IR spectrum: 1 601 (C=N), 1 580 (furan or pyridine rings). ^{1}H NMR spectrum: 2.15 s, 3 H (Me-4a); 6.49 s, 1 H (H-3a); 6.66 d, 1 H, *J* = 5.1 (H-5a); 6.74 s, 1 H (H-4b); 7.12 s, 5 H (Ph); 7.21–7.49 m, 8 H (Ph); 7.82 d, 2 H, *J* = 7.1 (*o*-Ph); 8.05 d, 1 H, *J* = 5.1 (H-6a). Satellites: 6.42 s; 6.86–7.21 m; 7.78 d, *J* ≈ 7; 8.14 d, *J* ≈ 8. ^{13}C NMR spectrum: 21.61 CH_3 (Me-4a), 107.63 CH, 117.26 CH, 120.69 CH, 124.88 CH, 128.00 CH, 128.74 CH, 128.78 CH, 129.25 CH, 130.23 CH, 130.38 C, 131.76 CH, 132.23 C, 132.74 C, 138.28 C, 143.51 C (C-5b), 148.45 CH (C-6a), 148.61 C (C-4a), 155.33 C (C-2b), 160.44 C (C-1), 163.91 C (C-2a). One signal is overlapped.

N-(3-Methylpyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3e**): yellow solid, m.p. 59–63 °C (dried in vacuo only). For $C_{29}H_{22}N_2O$ (414.5) calculated: 84.03% C, 5.35% H, 6.76% N; found: 83.79% C, 5.58% H, 6.52% N. IR spectrum: 1 608 (C=N), 1 577 (furan or pyridine rings). ^{1}H NMR spectrum: 2.13 s, 3 H (Me-3a); 6.75 s, 1 H (H-4b); 6.79 dd, 1 H, *J* = 7.1 and 5.0 (H-5a); 7.09 s, 5 H (Ph); 7.80 d, 2 H, *J* = 7.1 (*o*-Ph); 8.07 d, 1 H, *J* ≈ 5. Satellites: 6.48 dd, *J* = 6.9 and 6.9; 6.90 s; 6.95 d, *J* = 7.6; 7.70–7.75 m; 7.91–7.96 m. ^{13}C NMR spectrum: 17.69 CH_3 (Me satellite, very weak), 18.03 CH_3 (Me-3a), 108.11 CH, 113.26 CH, 119.79 CH, 122.28 C, 123.09 CH, 124.80 CH, 125.39 C, 127.88 CH, 128.50 CH, 128.56 CH, 128.83 CH, 128.92 CH, 128.98 CH, 129.22 CH, 129.29 CH, 129.34 CH, 129.63 CH, 129.93 CH, 130.17 CH, 130.29 C, 130.60 CH, 131.38 CH, 132.46 C, 132.90 C, 133.52 CH, 135.01 C, 136.75 C, 138.16 CH, 138.26 CH, 141.84 C, 143.62 C, 146.23 CH, 155.35 C (C-2b), 159.19 C (C-1), 162.83 C (C-2a). Three C signals and ten CH signals are satellite signals.

N-(5-Phenylpyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3f**): yellow crystals, m.p. 160–162 °C (benzene). For $C_{34}H_{26}N_2O$ (478.6) calculated: 85.33% C, 5.48% H, 5.85% N; found: 85.21% C, 5.66% H, 5.62% N. IR spectrum: ≈1 600 (sh) (C=N), 1 577 and 1 588 (furan and pyridine rings). ^{1}H NMR spectrum: 6.65 d, 1 H, *J* = 7.9 (H-3a); 6.80 s, 1 H (H-4b); 7.08–7.52 m, 16 H (Ph); 7.14 s, 5 H (Ph); 7.52–7.59 m, 2 H (Ph); 7.74–7.80 m, 2 H (*o*-Ph); 7.93–8.00 m, 2 H (*o*-Ph). Satellites: 6.59 d, *J* = 7.9; 6.91–7.07 m; 7.81–7.89 m. ^{13}C NMR spectrum: 107.45 CH, 115.33 CH, 116.47 CH, 124.92 CH, 127.65 CH, 128.06 CH, 128.50 CH, 128.81 CH, 128.86 CH, 128.90 CH, 128.97 CH, 129.16 CH, 129.32 CH, 130.31 CH, 130.47 C, 131.39 C, 132.05 CH, 132.56 C, 138.26 CH, 139.96 C, 143.96 C (C-5b), 155.38 C (C-2b), 156.65 C (C-6a), 161.36 C (C-1), 163.43 C (C-2a). One signal is overlapped.

N-(5-Iodopyridin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine (**3g**): yellow crystals, m.p. 169–171 °C (benzene–heptane). For $C_{28}H_{19}IN_2O$ (526.4) calculated: 63.89% C, 3.64% H, 5.32% N, 24.11% I; found: 63.71% C, 3.86% H, 5.13% N, 24.02% I. IR spectrum: ≈1 600 (sh) and 1 595 (furan and pyridine rings). ^{1}H NMR spectrum: 6.49 d, 1 H, *J* = 8.2 (H-3a); 6.78 s, 1 H (H-4b); 7.06–7.21 m, 5 H (Ph); 7.27–7.53 m, 8 H (Ph); 7.66 dd, 1 H, *J* = 8.2 and ≈ 2.2 (H-4a); 7.85 d, 2 H, *J* = 7.7 (*o*-Ph); 8.39 s, 1 H (H-6a). ^{13}C NMR spectrum: 86.84 C (C-5a), 108.02 CH, 118.73 CH, 124.90 CH, 128.19 CH, 128.76 CH, 129.08 CH, 129.38 CH, 130.12 C, 130.32 CH, 132.00 CH, 132.54 C, 133.03 C, 137.99 C, 142.83 C (C-5b), 145.29 CH (C-4a), 154.56 CH (C-6a), 155.75 C (C-2b), 160.73 C (C-1), 162.79 C (C-2a).

Photoisomerization of Compound **4**

A solution of (*Z*)-ketone **4** (ref.[22], 17 mg, 34 μmol) in toluene (5 ml) was irradiated under stirring with a 200 W tungsten incandescent lamp at 45 °C and the reaction was monitored by TLC (silica gel, chloroform–ether 9 : 1). After 2.5 h the solvent was evaporated and the residue was chromatographed on a small silica gel column (5 g, 100/160 μm). Collected yellow fractions afforded 15 mg (88%) of *N-(benzo[h]quinolin-2-yl)-[(3,5-diphenylfuran-2-yl)phenylmethylidene]amine* (**5**), m.p. 240–241 °C (ethanol). For $C_{36}H_{24}N_2O$ (500.6) calculated: 86.38% C, 4.83% H, 5.60% N; found: 86.40% C, 4.90% H, 5.70% N. ^{1}H NMR spectrum: 6.63 s, 1 H (H-4b); 6.95 d, 1 H, *J* = 8.3 (H-3a); 6.97–7.10 m, 4 H; 7.12–7.30 m, 4 H; 7.33–7.51 m, 7 H; 7.55 d, 1 H, *J* = 8.9 (H-7a); 7.67 d, 1 H, *J* = 8.7 (H-6a); 7.81 d, 1 H, *J* = 7.9 (H-9a); 7.89 d, 1 H, *J* = 8.4 (H-4a); 7.99 d, 2 H, *J* = 7.4 (*o*-Ph); 8.92 d, 1 H, *J* = 8.3 (H-12a). ^{13}C NMR spectrum ($(CD_3)_2SO_4$): 107.22 CH (C-4b), 116.24 CH (C-3a), 123.08 C (C-5a), 123.81 CH, 124.77 CH, 125.18 CH, 125.77 CH, 126.18 CH, 127.36 CH, 127.47 CH, 127.63 CH, 127.88 CH, 128.05 CH, 128.18 CH, 128.25 CH, 128.55 CH, 128.60 CH, 129.08 CH, 129.17 CH, 129.23 CH, 129.91 C, 130.50 C, 131.22 C, 131.85 CH (*p*-Ph1), 133.28 C, 136.54 C, 137.43 CH (C-4a), 142.40 C, 144.35 C (C-14a), 153.85 C (C-2a), 160.18 C (C-1), 161.19 C (C-1). Four CH signals are overlapped.

X-Ray Analysis of Compound **3g**

The iodo derivative **3g**, $C_{28}H_{19}IN_2O$ (526.38), monoclinic system, space group $P2_1/n$ (No. 14), a = 11.503(2) Å, b = 21.323(6) Å, c = 10.209(2) Å, V = 2 381.2(9) $Å^3$, Z = 4, D_{calc} = 1.468 g cm^{-3}, $\mu(CuK\alpha)$ = 10.83 mm^{-1}, F(000) = 1 048.

The structure was solved by direct methods and subsequent Fourier techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F values. Empirical absorption correction (ref.[16]) was applied. The hydrogen atoms were placed in positions found from ideal geometry with $U_{iso} = U_{eq}$ of the neighbour carbons. Data collection and structure refinement parameters are listed in Table VI. Final coordinates and thermal parameters are given in Table VII. Table VIII shows some selected bond distances and angles supplying the molecular shape pictured in Fig. 1.

CALCULATIONS

The molecular geometries of structures **1a–3a**, and **6a** in the ground states were obtained by the PM3 (refs[10,11]) optimizations. A modified MECI (multielectron configuration interaction using active space of 10 occupied and 10 unoccupied MO's) procedure (ref.[12]) was used for calculations of excited states of the molecules.

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