^{13}C NMR AND IR STUDY OF SUBSTITUTION EFFECTS AND MASS SPECTRA OF BIPHENYL ANALOGUES OF α-CYANOCHALCONES

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Received November 29th, 1982

Thirteen biphenyl analogues of α-cyanochalcones *IIa*—*IIm* were prepared by condensation of *p*-phenylbenzoylacetonitrile (*I*) with *p*-substituted benzaldehydes. Their ^{13}C NMR chemical shifts were measured and correlated with the Hammett parameters (σ, σ^+) and the Swain–Lupton reactivity parameters. A consistent picture of the transmission of the substituent (electronic) effects through the carbon skeleton of the studied compounds was obtained. The relationship between the structure of synthetized α-cyanochalcones and their mass spectra is discussed.

Correlation of substituent effects and ^{13}C NMR chemical shifts had attracted a considerable attention. Even if the limiting role of various effects was pointed out[1,2], it seems that the charge densities are the principal determinants of the chemical shifts. The analysis of these correlations in series of compounds where other factors are constant might provide the information on the transmission of electronic effects and on the electron density distribution, especially in π-electron systems. The best results were obtained for styrenes[3,4], chalcones[5], and for mono-[6] and disubstituted benzenes[7]. During the study of chemical reactivity of compounds containing the conjugated system —CO—C(CN)=CH— were prepared the biphenyl analogues of α-cyanochalcones *IIa*–*IIm*. These π-electron rich compounds represent interesting systems for the study of the substitution effects. The goal of this study was to measure the ^{13}C NMR chemical shifts in compounds *IIa*–*IIk*, to determine the extent to which they reflect the electron distribution and to interpret the mechanism of the transmission of the substituent effects in these compounds using both one-parameter correlation (σ, σ^+) and dual parameter approach (F and R). We also attempted to interpret the mass spectra of compounds *IIa*, *IIb*, *IIf*, *IIi*, and *IIk*.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined on a Boetius apparatus. The spectra were measured on the instruments Perkin–Elmer 325 (IR), Carl Zeiss Jena Specord UV VIS (UV), Varian XL-100 (^{1}H NMR), and LKB 9000 (70 eV, mass spectra). ^{13}C NMR spectra were recorded on a Tesla BS 567 Fourier Transform NMR spectrometer in saturated

C^2HCl_3 solutions; APT technique was employed. Negligible concentration effects (see[8]) were assumed. Chemical shifts (±0·1 ppm) are related to tetramethylsilane. Experimental parameters were: observing frequency 25·14 MHz, digital resolution 1·05 Hz, pulse width 3 μs (30°), pulse repetition 3 s, temperature 30°C).

p-*Phenylbenzoylacetonitrile* (I) was prepared by condensation of ethyl 4-biphenylcarboxylate with acetonitrile in the presence of sodium hydride, m.p. 113—114°C (ethanol); lit.[9] gives 112 to 113°C. Compounds *IIa—IIm* were prepared by condensation of corresponding p-XC_6H_4CHO with ketonitrile *I* according to ref.[10].

Synthesis of α-caynochalcones *IIa—IIm*

Piperidine (3 drops) was added to the suspension of *p*-phenylbenzoylacetonitrile (*I*, 0·005 mol) and corresponding benzaldehyde (0·005 mol) in ethanol (15 ml). The mixture was stirred 6 h at the room temperature then refluxed 30 min and allowed to stand overnight. The precipitate was filtered and crystalized from a suitable solvent to the constant melting point. The synthetized derivatives *IIa—IIm* and their spectroscopic properties are summarized in Tables I and II.

Mass spectra (ions and % of relative intensity). *IIa*: 310 (13), 309 (51), 308 (12), 282 (6), 232 (2), 231 (4), 182 (16), 181 (100), 154 (12), 153 (30), 152 (43), 151 (13), 127 (7), 126 (4), 101 (7), 78 (9), 77 (13), 76 (6), 75 (5), 63 (3), 52 (4), 51 (9), 50 (4). *IIb*: 380 (48), 365 (100), 353 (5), 336 (3), 232 (2), 182 (6), 181 (40), 154 (5), 153 (22), 152 (26), 151 (9), 127 (6), 126 (3), 101 (3), 78 (23), 77 (10), 76 (6), 75 (3), 68 (6), 63 (4), 52 (6). *IIf*: 351 (25), 336 (6), 324 (5), 309 (13), 308 (40), 232 (4), 231 (3), 182 (16), 181 (100), 168 (4), 154 (7), 153 (33), 152 (40), 151 (12), 127 (8), 126 (3), 101 (3), 78 (3), 77 (7), 76 (4), 75 (3), 63 (4), 51 (5). *IIi*: 345 (12), 343 (32), 318 (3), 316 (5), 307 (5), 232 (2), 231 (3), 182 (16), 181 (100), 154 (18), 153 (31), 152 (44), 151 (14), 127 (9), 126 (6), 102 (4), 101 (3), 77 (5), 76 (4), 75 (6), 63 (3), 51 (5). *IIk*: 354 (36), 327 (2), 324 (7), 232 (1), 231 (1), 182 (15), 181 (100), 154 (6), 153 (31), 152 (41), 151 (13), 127 (7), 126 (5), 101 (3), 77 (6), 76 (6), 75 (4), 63 (64), 51 (6), 50 (4).

RESULTS AND DISCUSSION

^{13}C NMR spectra of all synthetized compounds indicate the presence of one isomer only. ^{13}C NMR chemical shifts of compounds *IIa—IIk* are given in Table III. Substituent chemical shifts (SCS) relative to the parent compound *IIa* are given in Table IV. The assignment of atoms C(7), C(8), C(9) and C(10) of the conjugated system —CO—C(CN)=CH— was unambiguous in all cases. The signal of C(10) carbonyl group was observed in the lowest field, that of C(8) at the highest field. The chemical shifts of these carbon atoms exhibit a slight difference ($\Delta\delta_{max}$ = 0·3 ppm) only from that of analogous signals in α-cyanochalcones[4]. This effect indicates a minimal contribution of the second ring in the biphenyl moiety to the electrone distribution in this conjugated system. The carbonyl group in biphenyl analogues partially blocks the electron transmission. Therefore, the biphenyl substitution effect is not observed and is reduced to the effect of a phenyl group[5]. Phenyl group carbon atoms were assigned using the additivity rules[11] and by comparison with signals of analogous atoms in the ^{13}C NMR spectra of chalcones[5]. This assignment was confirmed by the characteristic carbon–fluorine coupling constants in compound *IIh*.

This compound was used as a model for the assignment of phenyl ring CH carbons that resonate in the same region as the skeleton biphenylene CH atoms in compounds *IIa*–*IIk*. Carbon atoms of 4-substituted biphenyl were assigned using the model

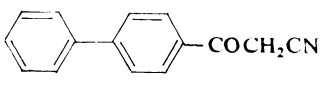
TABLE I

Biphenyl analogues of α-cyanochalcones *IIa*–*IIm*

Compound (yield, %)	X	M.p., °C (solvent)	Formula (m.w.)	Calculated/Found		
				% C	% H	% N
IIa	H	164–166	$C_{22}H_{15}NO$	85,40	4·90	4·53
(68)		(C_2H_5OH–C_6H_6)	(309·4)	85·37	4·98	4·48
IIb	$N(C_2H_5)_2$	174–175	$C_{26}H_{24}N_2O$	82·06	6·37	7·36
(75)		(i-C_3H_7OH–C_6H_6)	(380·5)	82·04	6·40	7·22
IIc	$N(CH_3)_2$	241–243	$C_{24}H_{20}N_2O$	81·78	5·73	7·95
(74)		(i-C_3H_7OH–C_6H_6)	(352·5)	81·76	5·98	7·90
IId	OC_2H_5	153–154	$C_{24}H_{19}NO_2$	81·55	5·43	3·96
(93)		(C_2H_5OH–C_6H_6)	(353·4)	81·62	5·54	3·81
IIe	OCH_3	152–154	$C_{23}H_{17}NO_2$	81·39	5·06	4·13
(88)		(C_2H_5OH–C_6H_6)	(339·4)	81·51	5·02	4·08
IIf	i-C_3H_7	115–116	$C_{25}H_{21}NO$	85·43	6·03	3·99
(58)		(i-C_3H_7OH–C_6H_6)	(351·5)	85·36	6·15	4·29
IIg	CH_3	166–168	$C_{23}H_{17}NO$	85·41	5·31	4·33
(84)		(C_2H_5OH–C_6H_6)	(323·4)	85·28	5·58	4·51
IIh	F	146–148	$C_{22}H_{14}FNO$[a]	80·71	4·32	4·28
(46)		(i-C_3H_7OH–C_6H_6)	(327·4)	81·04	4·33	4·16
IIi	Cl	137–138	$C_{22}H_{14}ClNO$[b]	76·85	4·11	4·07
(64)		(i-C_3H_7OH)	(343·8)	76·80	4·03	4·20
IIj	I	160–163	$C_{22}H_{14}INO$	60·70	3·25	3·22
(81)		(i-C_3H_7OH–C_6H_6)	(435·3)	60·81	3·23	3·15
IIk	NO_2	160–162	$C_{22}H_{14}N_2O_3$	74·55	3·99	7·91
(35)		(C_2H_5OH–C_6H_6)	(354·4)	74·51	4·08	7·87
IIl	OH	217–219	$C_{22}H_{15}NO_2$	81·20	4·65	4·31
(86)		(C_2H_5OH–DMF)[c]	(325·4)	81·24	4·87	4·24
IIm	$NHCOCH_3$	220–222	$C_{24}H_{18}N_2O_2$	78·66	4·96	7·65
(69)		(CH_3CN)	(366·4)	78·31	4·97	7·72

[a] Calculated: 5·80% F, found: 6·30% F; [b] calculated: 10·31% Cl, found: 10·28% Cl; [c] DMF dimethylformamide.

compound *IIh* and the comparison with spectra of 4-substituted biphenyl derivatives[12].



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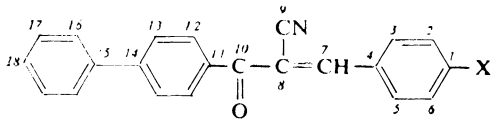
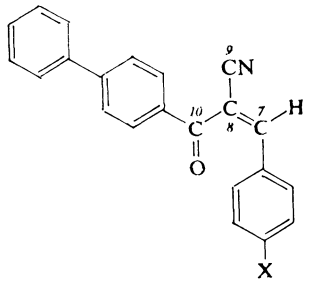


IIa, X = H
IIb, X = $(C_2H_5)_2N$
IIc, X = $(CH_3)_2N$
IId, X = C_2H_5O
IIe, X = CH_3O
IIf, X = $(CH_3)_2CH$
IIg, X = CH_3
IIh, X = F
IIi, X = Cl
IIj, X = I
IIk, X = NO_2
III, X = HO
IIm, X = CH_3CONH



III

Comparing the chemical shifts of C(1) and C(4) atoms of the phenyl ring in compounds *IIa*–*IIk* with the corresponding chemical shifts in *E*-chalcones, an interesting phenomenon becomes apparent. The signals of C(1) are shifted in average of 2·85 ppm downfield and that of C(4) of 2·78 ppm upfield with respect to the chalcones[5]. Even more remarkable changes can be observed for C(7) (average upfield shift 10·44 ppm) and C(8) (downfield shift 12·00 ppm). Therefore, the substitution of hydrogen atom for C≡N group results in marked separation of the electron densities localized at centers C(1), C(4), C(7) and C(8) in the biphenyl analogues of α-cyanochalcones *IIa*–*IIk*. Correlations of ^{13}C NMR chemical shifts with Hammett parameters σ (Table V) show that the C(8) atom of the ethylenic bond is the most sensitive to the substitution effect (ϱ = 7·662) and gives a correlation coefficient r = 0·942 (N = 10). This effect is in agreement with the observation made on the chalcone derivatives[5]. A slightly higher coefficient of correlation r = 0·953 was obtained for atom C(7) but with the slope of a reversed sign. This fact reflects the polarity of a double bond substituted by the C≡N and C=O groups. The polarity is caused by a marked decrease of the electron density at C (8) and by resulting decrease in the effective screening of this atom. A very tight correlation was obtained for the carbonyl

group carbon, C(10): $r = 0{\cdot}992$; on the contrary to chalcones[5], their furane and thiophene analogues[13,14] for which the correlation of SCS with σ constants was not observed. This fact is also reflected by the relationship between $\Delta\delta$C(10) and $\Delta\delta$(C=O). The transmission of the substitution effect on C(10) is apparently caused by an electronacceptor effect of the C≡N group and therefore the carbonyl group that is attached to the same carbon C(8) becomes more sensitive to the substitution in the *para*-position. An alternative explanation is based on the geometric arguments. Marked difference in chemical shifts of atoms C(1), C(2) and C(3) of the phenyl group in compounds *IIa*–*IIk* on the contrary to the analogous signals in chalcones (*E*-isomers) might be due in the structure *III* to the diamagnetic screening of these positions by the carbonyl group. Assuming the planarity of compounds *II* and the rotation around the C(8)–C(10) bond and the *E*–*Z* isomerism on the double bond

TABLE II

Spectral characteristics of α-cyanochalcones *IIa*–*IIm*

Compound	δ_H, ppm ($CDCl_3$)		$\tilde{\nu}_{max}$, cm^{-1}		λ, nm (C_2H_5OH) λ_{max} (log ε)
	δ(X)	δ(H-arom.)	ν(C≡N)[a]	ν(C=O)[a]	
IIa	—	7·40–8·18 m	2 207	1 666	294 (4·38)
IIb	1·21 t (CH_3) 3·46 q (CH_2)	7·30–8·16 m 6·68 d (H_{ortho})	2 200	1 650	458 (4·71)
IIc	3·11 s (CH_3)	7·29–8·11 m 6·69 d (H_{ortho})	2 205	1 647	450[b] (—[b])
IId	1·46 t (CH_3) 4·12 q (CH_2)	7·26–8·18 m 6·98 d (H_{ortho})	2 209	1 662	361 (4·36)
IIe	3·88 s	7·30–8·20 m 7·00 d (H_{ortho})	2 204	1 664	359 (4·16)
IIf	1·28 d (CH_3) 2·97 m (CH)	7·30–8·20 m	2 209	1 668	325 (4·39)
IIg	2·42 s (CH_3)	7·30–8·22 m	2 216	1 664	301 (4·41)
IIh	—	7·16–8·20 m	2 212	1 666	289 (4·30)
IIi	—	7·36–8·16 m	2 218	1 668	291 (4·34)
IIj	—	7·30–8·10 m	2 211	1 668	284 (4·48)
IIk	—	7·36–8·48 m	2 218	1 672	282 (4·44)
III	—	7·28–8·12 m 6·92 d (H_{ortho})	2 209	1 665	369 (4·47)
IIm	2·04 s (CH_3)[c]	7·28–8·14 m[c]	2 220	1 666[d]	360 (4·32)

[a] Compounds *IIa*–*IIk* were measured in chloroform, compounds *III* and *IIm* in KBr pellets; [b] measured as a saturated solution in ethanol; [c] measured in hexadeuteriodimethyl sulphoxide; [d] 1 710 cm^{-1} ν(C=O) of the $NHCOCH_3$ group.

it is possible to derive 4 conformational isomers (*E* and *Z* isomers, each in two conformations). The PPP calculation[15] showed that the relative π-electron energy of the structure *III* is the lowest among all conformers. The observed tight correlation might be due to a marked influence on the substitution effect through space caused by a relatively small distance between the substituent X and the C=O group.

On the contrary to an earlier work[16], no unambiguous Hammett dependence of the C=O stretching mode on the σ parameter was observed. The reason for this phenomenon is evidently the conformational and/or configurational nonhomogeneity of the investigated compounds under the conditions of measurement. As the consequence of all those mentioned facts, the correlation $\Delta\delta\ C(10) = a\ \Delta\nu(C{=}O) + b$ (Fig. 1) is evidently not fulfilled for all points (substituents not included are: *i*-C_3H_7, $(CH_3)_2N$, $(C_2H_5)_2N$).

Satisfactory correlation coefficients were obtained for C(9), C≡N group and for the quaternary atoms C(11), C(14) and C(15). However, the substituent effect on C(14) and C(15), respectively, cannot be meaningful since the difference in SCS is

TABLE III

^{13}C NMR chemical shifts of compounds *IIa*—*IIk*. Data in ppm with respect to tetramethylsilane, saturated solutions in deuteriochloroform

Carbon	*IIa*	*IIb*	*IIc*	*IId*	*IIe*	*IIf*
C(1)	133·27	152·13	154·00	163·63	164·20	[a] —
C(2, 6)	131·18	111·57	119·94	115·49	115·04	131·55
C(3, 5)	129·42	143·91	134·58	133·94	133·87	127·55
C(4)	132·26	[b] —	[b] —	124·88	125·05	129·79
C(7)	155·16	155·46	155·60	155·16	155·04	155·34
C(8)	110·71	101·26	102·81	106·86	107·12	109·10
C(9)	116·98	119·52	120·38	117·92	117·84	117·32
C(10)	188·17	189·41	189·30	188·70	188·66	188·44
C(11)	134·76	136·37	136·34	135·29	135·25	134·80
C(11)	134·76	136·37	136·34	135·29	135·25	134·80
C(12)	130·13	129·68	129·79	129·98	129·98	130·03
C(13)	127·44	127·03	127·18	127·29	127·29	127·25
C(14)	146·49	145·15	145·39	146·15	146·08	146·08
C(15)	139·88	140·10	140·30	140·04	139·95	140·02
C(16)	127·44	127·33	127·44	127·40	127·37	127·32
C(17)	129·12	129·01	129·09	129·12	129·12	129·08
C(18)	128·56	128·26	128·23	128·45	128·45	128·45
others	—	12·59	40·04	14·60	55·69	23·53
		44·86		64·17		34·40

TABLE III
(*Continued*)

Carbon	*IIg*	*IIh*	*IIi*	*IIj*	*IIk*
C(1)	144·74	165·30[c]	[d] —	100·77	149·82
C(2, 6)	131·36	117·28[e]	129·79	138·76	124·42
C(3, 5)	130·17	133·90[f]	132·25	132 04	131·51
C(4)	129·50	128·41	130·58	131·40	137·53
C(7)	155·38	153·89	153·55	153·85	151·79
C(8)	109·14	110·00	110·90	111·01	114·22
C(9)	117·32	117·10	116·83	116·76	116·16
C(10)	188·44	188·02	187·76	187·73	187·05
C(11)	134·84	134·54	134·46	134·35	133·75
C(12)	130·01	130·09	130·09	130·06	130·24
C(13)	127·29	127·44	127·37	127·33	127·40
C(14)	146·19	146·49	146·49	146·45	147·01
C(15)	139·81	139·73	139·66	139·62	139·47
C(16)	127·37	127·44	127·37	127·33	127·55
C(17)	129·09	129·16	129·12	129·09	129·16
C(18)	128·45	128·60	128·60	128·56	128·75
others	21·81	—	—	—	—

[a] Signal was not observed probably due to the overlap with the signal of C(14), $\delta = 146{\cdot}08$ ppm; [b] signals falling into the narrow range of aromatic CH's and their identification was not possible; [c] J(C—F) = 267·4 Hz; [d] signal was not observed probably owing to its overlap with the signal of C(9), $\delta = 134{\cdot}46$ ppm; [e] J(C—F) = 22·5 Hz; [f] J(C—F) = 9·7 Hz.

small (about 1 ppm). The results of correlations with σ^+ parameters[17] (Table V) show that a higher correlation coefficient was obtained for C(8) and C(9) and a lower one for atoms C(7) and C(10). The correlations with σ and σ^+ are comparable in the case of atoms C(11), C(14), and C(15) in biphenyl rest. When comparing the slopes of the correlations of SCS with Hammett σ and σ^+ parameters, we note that the slope (ϱ) changes alternatively its sign when going from one quaternary carbon atom to the another along all molecular skeleton. Biphenyl analogues of α-cyanochalcones II therefore represent an illustrative example of so-called "reversed" correlations, first time observed by Bromilow and Brownlee[18] in *meta- and para*-substituted benzonitriles. It was stressed out[4] that the "reversed" correlations are a characteristic feature of compounds in which π-electrons densities play a dominant role in the determination of the screening at the given site of the molecule. Our results agree with such a picture.

Very tight correlations were found for ^{13}C NMR chemical shifts of atoms C(7), C(8), C(9), C(10), C(11), C(14) and C(15) against the values measured on analogically

substituted chalcones and α-cyanochalcones (Table V). The numbering system of carbon atoms in these compounds was taken from the refs[4,5]. The results of correlations indicate a similar localization of electron densities at the corresponding centers in these systems. To obtain the information on the formal inductive (field) effect of the X substituent to the chemical shifts, the correlation using Swain–Lupton parameters F and R in the dual parameter approach[19] was performed. Table VI illustrates the results obtained for the *para*-substituted α-cyanochalcones *IIa*–*IIk*. Tight correlations were found for atoms C(7), C(8), C(11) and C(14). The best correlation

TABLE IV

Relative ^{13}C NMR chemical shifts ($\Delta\delta$, ppm) of quaternary carbons in compounds *IIb*–*IIk* relative to the unsubstituted compound *IIa*

Compound	C(1)	C(4)	C(7)	C(8)	C(9)	C(10)	C(11)	C(14)	C(15)
IIb	18·86	—	0·30	−9·45	2·54	1·24	1·61	−1·34	0·22
IIc	20·73	—	0·44	−7·90	3·40	1·13	1·58	−1·10	0·42
IId	30·36	−7·38	0·00	−3·85	0·94	0·53	0·53	−0·34	0·16
IIe	30·93	−7·21	−0·12	−3·59	0·86	0·49	0·49	−0·41	0·07
IIf	—	−2·47	0·18	−1·61	0·34	0·27	0·04	−0·41	0·14
IIg	11·47	−2·76	0·22	−1·57	0·34	0·27	0·08	−0·30	−0·07
IIh	37·46	−3·85	−1·27	−0·71	0·12	−0·15	−0·23	0·00	−0·15
IIi	—	−1·68	−1·61	0·19	−0·15	−0·41	−0·30	0·00	−0·22
IIj	−32·50	−0·86	−1·31	0·30	−0·22	−0·44	−0·41	0·00	−0·26
IIk	16·53	5·27	−3·37	3·51	−0·82	−1·12	−1·01	0·52	−0·41

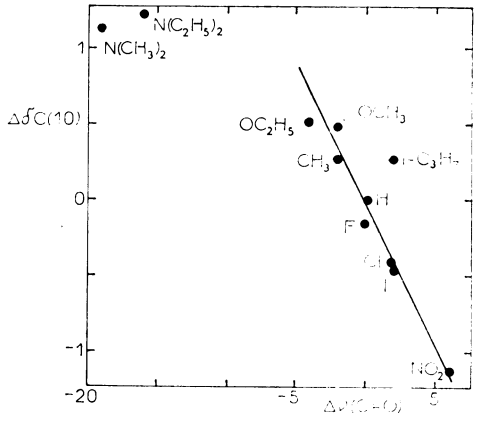


FIG. 1

^{13}C NMR SCS of atom C(10) against the corresponding values of the C=O bond valence vibrations in compounds *IIa*–*IIk* $\Delta\delta C(10) = \delta C(10)_X - \delta C(10)_H$, $\Delta\nu(C{=}O) = \nu(C{=}O)_X - \nu(C{=}O)_H$

(r = 0·989, N = 10) was again obtained for the atom C(10) of the carbonyl group and the poorest one for C(9) of the C≡N group. The correlations for C(14) and C(15) are less meaningful for the reasons mentioned above. From the correlations with parameters F and R it follows that the inductive effect brings the largest contribution to the chemical shift of the C(7) atom and the resonance effect should mainly influence the π-electron density at C(8) and C(11) atoms.

TABLE V

Correlation of ^{13}C NMR chemical shifts of compounds *IIa*—*IIk* (see Table IV) with Hammett parameters (σ, σ^+) and with relative ^{13}C NMR chemical shifts of chalcones[5] and α-cyanochalcones[4]

Carbon	Parameter	ϱ^a	$\delta_0{}^b$	r^c	N^d
C(7)	σ	−2·957 (0·355)	−0·786 (0·403)	0·953	9[e]
	σ^+	−1·485 (0·379)	−1·204 (0·744)	0·829	9[e]
	$\Delta\delta$C(β)[f]	0·992 (0·085)	−0·232 (0·281)	0·982	7
	$\Delta\delta$C(β)[g]	0·968(0·022)	0·111 (0·075)	0·999	7
C(8)	σ	7·662 (0·962)	−1·462 (1·091)	0·942	10
	σ^+	4·619 (0·186)	−0·281 (0·368)	0·994	10
	C(α)[f]	−1·268 (0·084)	−0·631 (0·573)	0·989	7
	C(α)[g]	0·917 (0·017)	−0·155 (0·163)	0·999	7
C(9)	σ	−1·538 (0·209)	0·246 (0·198)	0·941	9[h]
	σ^+	−1·182 (0·082)	0·027 (0·106)	0·984	9[h]
	$\Delta\delta$C(≡N)[g]	1·377 (0·060)	0·103 (0·144)	0·995	7
C(10)	σ	−1·650 (0·072)	0·044 (0·081)	0·992	10
	σ^+	−0·912 (0·094)	−0·188 (0·186)	0·960	10
	$\Delta\delta$C(=O)[f]	1·651 (0·489)	0·343 (0·429)	0·834	7
	$\Delta\nu$(C=O)[i]	−0·187 (0·066)	−0·034 (0·454)	0·987	7[j]
C(11)	σ	−1·717 (0·222)	0·063 (0·252)	0·939	10
	σ^+	−1·035 (0·054)	−0·201 (0·106)	0·989	10
	$\Delta\delta$C(1′)[f]	1·828 (0·078)	−0·075 (0·083)	0·995	7
C(14)	σ	1·054 (0·132)	−0·196 (0·149)	0·943	10
	σ^+	0·624 (0·049)	−0·036 (0·098)	0·976	10
	$\Delta\delta$C(4′)[f]	1·250 (0·138)	−0·161 (0·132)	0·971	7
C(15)	σ	−0·602 (0·078)	−0·037 (0·088)	0·939	10
	σ^+	−0·339 (0·049)	−0·123 (0·097)	0·927	10

[a] Slope, standard error in parentheses; [b] intercept on the δ-axis, standard error in parentheses; [c] correlation coefficient; [d] number of substituents in the regression analysis; [e] H omitted; [f] chalcones; [g] α-cyanochalcones; [h] $(CH_3)_2N$ omitted; [i] relative wavenumbers with respect to compound *IIa* obtained from the IR spectra; [j] substituents $(CH_3)_2CH$, $(CH_3)_2N$, and $(C_2H_5)_2N$ were omitted.

Mass spectra of α-cyanochalcones have not been reported yet. Mass spectra of biphenyl analogues of α-cyanochalcones *IIa*, *IIb*, *IIf*, *IIi*. and *IIk* can be interpreted in terms of two main fragmentation modes *A* and *B*. Relatively intensive molecular ion

TABLE VI

Correlation of relative ^{13}C chemical shifts of α-cyanochalcones *IIa*, *IIc*—*IIk* with inductive (F) and resonance (R) substituent parameters[a]

Atom	f[b]	r'[b]	δ_0[b]	r[c]	N[d]	% R[e]
C(7)	−2·380	−1·672	−0·180	0·977	10	33·97
C(8)	3·118	−10·113	−0·360	0·969	10	70·37
C(9)	−1·075	−3·347	0·112	0·869	10	69·51
C(10)	−0·924	−1·680	0·016	0·989	10	57·11
C(11)	−0·826	−2·022	−0·080	0·948	10	64·19
C(14)	0·576	1·126	−0·160	0·952	10	58·87
C(15)	−0·373	−0·540	−0·017	0·935	10	51·46

[a] Substituent parameters F and R taken from[19], the values for substituents $(CH_3)_2CH$ and $(CH_3)_2N$ were calculated from the σ_p and σ_m values using the equation given in this work; [b] coefficients in the equation $\Delta\delta = fF + r'R + \delta_0$; [c] correlation coefficient; [d] number of substituents included in the regression analysis; [e] % of resonance contribution, calculated according to ref.[19].

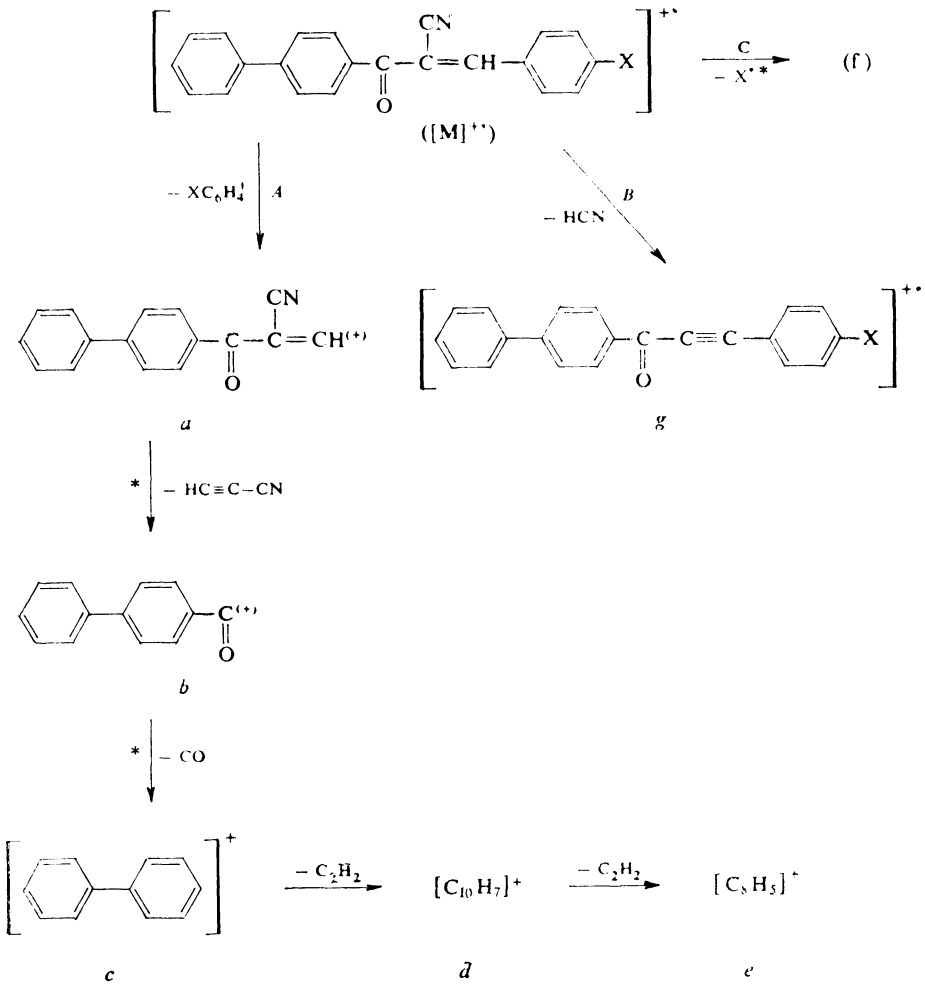
TABLE VII

Important ions present in the mass spectra of compounds *IIa*, *IIb*, *IIf*, *IIi*, and *IIk*; *m/z* (% of relative intensity)

Ion	*IIa*	*IIb*	*IIf*	*IIi*	*IIk*
$[M]^{+\cdot}$	309 (51)	380 (40)	351 (25)	345 (12) 343 (32)	354 (36)
$[a]^+$	232 (2)	232 (2)	232 (4)	232 (2)	232 (1)
$[b]^+$	181 (100)	181 (40)	181 (100)	181 (100)	181 (100)
$[c]^+$	153 (30)	153 (22)	153 (33)	153 (31)	153 (31)
$[d]^+$	127 (7)	127 (6)	127 (8)	127 (9)	127 (7)
$[e]^+$	101 (7)	101 (3)	101 (3)	101 (3)	101 (3)
$[f]^+$	—	365 (100)[a]	308 (40)	307 (5)[b]	324 (7)[c]
$[g]^{+\cdot}$	282 (6)	353 (5)	324 (5)	318 (3) 316 (5)	327 (2)

[a] Ion $[M - CH_3]^+$; [b] ion $[M - HCl]^{+\cdot}$; [c] ion $[M - NO]^+$.

$[M]^{+\bullet}$ that can be observed in the spectra of compounds *IIa*, *IIb*, *IIf*, *IIi*, and *IIk* can either lose a phenyl ring with the attached X substituent in the *para*- position what leads to the formation of a rather unstable ion *a*, *m/z* 232 or undergo an elimination of HCN under formation of the ion *g*. The unstable ion *a* produces by loss of HC≡CCN an ion *b*, *m/z* 181, a basis peak in all mass spectra except the compound *IIb*. This ion undergoes further fragmentation and gives rise to ions *c*, *m/z* 153 $[b - CO]^+$, *d*, *m/z* 127 $[c - C_2H_2]^+$, and *e*, *m/z* 101 $[d - C_2H_2]^+$. Ions *d* and *e* that arise by subsequent elimination of acetylene from the ion *c* are the characteristic fragment ions for the aromatic compounds, *i.e.* biphenyl in our case[20]. The third



SCHEME 1 (X = H, $N(C_2H_5)_2$, i-C_3H_7, Cl, NO_2)

fragmentation mode *C* (Scheme 1) represents the fragmentation of the phenyl ring substituent.

The fragmentation processes *A* and *B* produce ions that are independent on the nature of the substituent X of the phenyl ring and give series of characteristic peaks which make this class of organic compounds easily identifiable (Scheme 1). Important ions present in the mass spectra of compounds *IIa*, *IIb*, *IIf*, *IIi*, and *IIk* are given in Table VII.

The authors thank to the members of Central laboratories of the Institute Dr E. Janečková, Dr A. Kohoutová (IR spectra measurement) and Dr P. Zachař (mass spectra measurement). Elemental analyses were performed in the Analytical laboratory (head: Dr L. Helešic).

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Translated by P. Sedmera.