SYNTHESIS OF 4,7-DIAMINO-3-FORMYLCOUMARINS AND AZOMETHINES DERIVED FROM THEM

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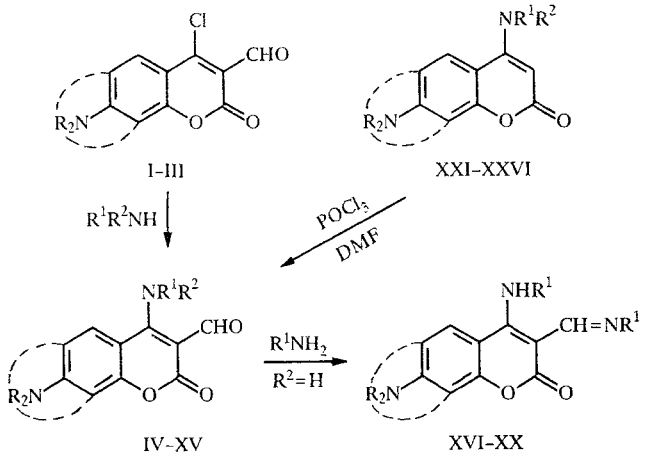
A series of 4,7-diamino-3-formylcoumarins has been synthesized by the reaction of 7-dialkylamino-4-chloro-3-formylcoumarins with primary and secondary amines and by the formylation of 4,7-diaminocoumarins by the Vilsmeier reaction. The corresponding Schiff's bases are formed by reaction with primary amines.

The aim of the present work was the synthesis of 4,7-diamno-3-formylcoumarins and of Schiff's bases derived from them which are of interest as potential chelate-forming compounds, photothermochromes [1], substances possessing pharmacological activity [2, 3], and also intermediates for obtaining new luminophores, fluorescing in the long-wave region of the visible spectrum [4].

We have therefore studied the reaction of the coumarins (I)-(III), obtained previously in [5], with t-butylamine, cyclohexylamine, benzylamine, aniline, diethylamine, piperidine, morpholine, and imidazole. A series of 4,7-diamino-3-formylcoumarins (IV)-(XV) has been obtained and in the case of primary amines and Schiff's bases (XVI)-(XX) were also isolated. The yields of the 4,7-bis-N,N-disubstituted derivatives (VIII)-(XII), (XIV), and (XV) were close to quantitative. The aldehyde:azomethine ratio for the primary amine derivatives (IV)-(VII), (XIII), and (XIV)-(XX) may shift in the direction of aldehyde or azomethine depending on the quantity and order of addition of the reactants (see Experimental, Table 1).



I, IV—XI, XVI—XIX, XXI—XXVI R = C_2H_5; II, XII R—R = $-(CH_2)_2O(CH_2)_2-$; III, XIII—XV, XX R = $-(CH_2)_3-$C-orthoIV—VII, XIII, XXI—XXIII R^2 = H; IV, XVI, XXI R^1 = t-C_4H_9; V, XVII, XXII R^1 = cyclo-C_6H_{11}; VI, XVIII, XXIII R^1 = $CH_2C_6H_5$; VII, XIII, XIX, XX R^1 = C_6H_5; VIII, XXIV R^1 = R_2 = C_2H_5; IX, XXV R^1—R^2 = $-(CH_2)_5-$; X, XII, XIV, XXVI R^1—R^2 = $-(CH_2)_2O(CH_2)_2-$; XI, XV NR^1R^2 = N-imidazolyl

An alternative way of obtaining the aldehydes (IV)-(XV) is by the direct formylation of the known 4,7-diaminocoumarins (XXI)-(XXVI) [6] using the Vilsmeier reaction. Such a possibility was already carried out by us previously in [5] for 4-benzylamino- and 4-morpholino-7-diethylamino-coumarins (XXIII) and (XXVI). In the present investigation we con-

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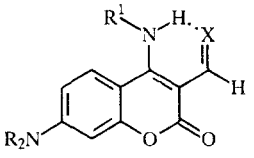
firmed that both reactions do occur with other 4,7-diaminocoumarins, but in this case the limiting factor may be the availability of the initial diaminocoumarin. For example, the reactivity of aniline is insufficient for the nucleophilic replacement of chlorine in 7-amino-4-chlorocoumarins, which are precursors of 4,7-diamino derivatives [6]. The overall yields of the desired compounds in the remaining cases calculated on the initial 7-amino-4-chlorocoumarins [7] were, as a rule, comparable in both methods used and were usually 40-60%.

The characteristics of compounds (IV)-(XX) are given in Tables 1-5. More detailed information on the coumarins (VI), (X), and (XII) were reported by us previously [5].

The assignment of signals in the PMR spectra of compounds (IV)-(XX) was made on the basis of known criteria [5, 8, 9]. However the establishment of the precise structure of the aminoaldehyde or azomethine portion in coumarins (IV)-(VII), (XIII), and (XVI)-(XX) was somewhat complex. In principle, compounds of that type may exist as different Z, E, and syn-, anti-isomers with an intramolecular hydrogen bond (IMHB) or without one, as in structures A-D.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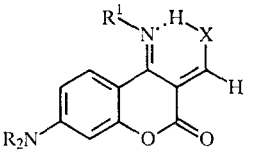
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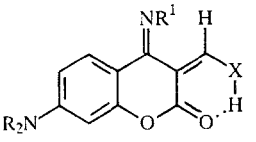
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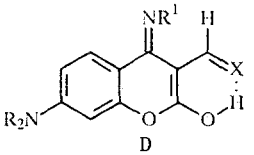
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The presence of an IMHB in compounds (IV)-(VII), (XIII), and (XVI)-(XX) was confirmed by the low field signal for the chelated proton at 12-14 ppm. The fact that the chemical shift (CS) of the methyl proton changes over a very small range in all the enumerated coumarins (Tables 2 and 3) indicates the commonality of structure of these compounds. In addition, since the CS of the aldehyde protons for all the formyl derivatives (IV)-(XV) practically coincide it may be assumed that the most probable form of compounds (IV)-(VII) are the isomers of type A. Similar conclusions are true for the azomethines (XVI)-(XX). The detection in the spectra of coumarins (V), (VI) [5], and (XVIII) of the characteristic splitting of the signals of the NH protons and of the α-CH or β-CH_2 groups of the substituent at position 4 ($^3J_{CH,NH}$ ~ 5-8 Hz) may serve to confirm this. The CS values of the chelated protons, typical of similar systems [10], and the sharp singlet form of the proton signals of the formyl or azomethine groups also point in favor of isomers of structure A for all the monoalkyl or phenylamino derivatives.* This conclusion was confirmed by the results of X-ray structural investigations of the coumarin (XIII). The overall form of this molecule is shown in Fig. 1. The presence of a phenylamino group leads to steric stress in the molecule, partially alleviated by turning the phenyl ring by 63.7° relative to the mean surface of the coumarin ring, and also by increasing the angles $C_{(4)}N_{(2)}C_{(16)}$ to 127.9° and $C_{(4a)}C_{(4)}N_{(2)}$ to 122.9°. In addition the contacts of $C_{(5)}-C_{(16)}$ (3.013 Å) and $C_{(5)}-C_{(21)}$ (3.187 Å) are significantly shortened. Probably stearic reasons also cause deformation of the coumarin ring itself which has a structure which is not completely flat. The dihedral angle between the two component rings is 5.2°.

The total of the angles at the $N_{(1)}$ atom is 359.3° showing its planar-trigonal configuration. The bond length of $C_{(7)}-N_{(1)}$ at 1.369 Å indicates the efficient conjugation of the $N_{(1)}$ unshared electron pair with the π-system of the carbocycle, the bond lengths of which have a quinoid character. The loss of uniformity of the bonds in its benzene ring (displayed most significantly in the lengthening of the $C_{(6)}-C_{(7)}$ bond to 1.430 Å from 1.368 Å in coumarin itself), observed in an unsubstituted coumarin molecule [11], was also observed in other 7-aminocoumarins [12, 13]. The distribution of bond lengths in each bicyclic coumarin system studied suggests the more preferred channel for charge transfer on excitation, from the amino group at position 7 to the carbonyl group, is determined by the chain $N^{\delta+}-C_{(7)}-C_{(8)}-C_{(8a)}-C_{(4a)}-C_{(4)}-C_{(3)}-C_{(2)}-O^{\delta-}$. This conclusion also applies generally to structure (XIII); however the structure of the latter has its own special features caused by the introduction into positions 3 and 4 of the coumarin ring of the accepting formyl and the donating phenylamino groups, respectively. The presence of these substituents causes a significant delocalization of the $X_{(3)}-C_{(4)}$ bond

*The authors are grateful to L. N. Kurkovskii for participating in discussions of the NMR spectra of these compounds.

TABLE 1. Physicochemical Characteristics of Coumarins (IX)-(XX)

Compound	Empirical formula	mp, °C	IR spectrum, $\nu_{C=O}$, cm^{-1}	R_f*	Yield, %
IV	$C_{18}H_{24}N_2O_3$	156	1690, 1650	0,39	84/80
V	$C_{20}H_{26}N_2O_3$	143	1700	0,63	88/83
VI***	$C_{21}H_{22}N_2O_3$	171	1705	0,42	86/85
VII	$C_{20}H_{20}N_2O_3$	229	1710	0,35	80
VIII	$C_{18}H_{24}N_2O_3$	110	1705, 1665	0,42	91/75
IX	$C_{19}H_{24}N_2O_3$	151	1705, 1665	0,46	89/79
X***	$C_{18}H_{22}N_2O_4$	182	1690	0,13	86/89
XI	$C_{17}H_{17}N_3O_3$	179	1760, 1730	0,07	94
XII***	$C_{18}H_{20}N_2O_5$	222	1690, 1665	0,04	84
XIII	$C_{22}H_{20}N_2O_3$	236	1710	0,28	72
XIV	$C_{20}H_{22}N_2O_4$	249	1685, 1650	0,15	90
XV	$C_{19}H_{17}N_3O_3$	217	1725, 1675	0,02	93
XVI	$C_{22}H_{33}N_3O_2$	91	1695	0,10	24
XVII	$C_{26}H_{37}N_3O_2$	95	1690	0,63	78
XVIII	$C_{28}H_{29}N_3O_2$	152	1680	0,46	36
XIX	$C_{26}H_{25}N_3O_2$	194	1690	0,60	86
XX	$C_{28}H_{25}N_3O_2$	218	1720	0,50	89

*The R_f values were measured on Silufol UV 254 plates in hexane–acetone, 3:1.

**The second number is the yield of product from the corresponding 4,7-diaminocoumarin (XXI)-(XXVI) (see Experimental).

***The physicochemical characteristics were in agreement with [5].

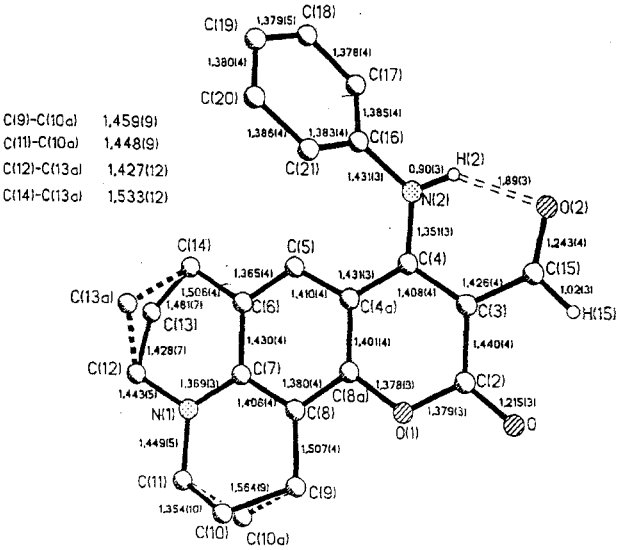

Fig. 1. Overall form of (XIII) with bond lengths.

in the α-pyrone ring, extended to 1.408 Å in comparison with the usual value (~1.34 Å) observed in related molecules with a free 3 position. This circumstance is caused by the strong conjugation within the chelate ring formed by the IMHB $N_{(2)}-H_{(2)}\ldots O_{(2)}$ [the $N_{(2)}$ to $O_{(2)}$ distance is 2.645 Å, the NHO angle is 140°]. This is also shown by the shortening of the $N_{(2)}-C_{(4)}$ bond to 1.351 Å compared with the $N_{(2)}-C_{(16)}$ bond length of 1.431 Å, the shortening of the $C_{(3)}-C_{(15)}$ bond to 1.426 Å compared with the standard 1.465 Å [14], and the lengthening of the $C_{(15)}-O_{(2)}$ bond to 1.243 Å against the standard 1.192 Å for aldehydes. There is an additional channel for charge transfer in (XIII) along the chain $N^{\delta+}{}_{(2)}-C_{(4)}-C_{(3)}-C_{(15)}-O_{(2)}{}^{\delta-}$ the atoms of which are located in one plane forming an angle of 3.7° with the plane of the α-pyrone ring.

TABLE 2. PMR Spectra of Coumarins (IV), (V), (VII)-(IX) and (XVI)-(XIX) in $CDCl_3$

Compound	Chemical shifts, δ, ppm (coupling constant, Hz)						
	5-H, (d 9,0)	6-H (d, d 9,0; 2,7)	8-H (d, 2,7)	3-CH= (s)	7-NCH_2 (q 7,0)	7-NCH_2CH_3 (t, 7,0)	other protons
IV	7,87	6,57	6,40	10,05	3,42	1,21	1,60 (9H, s, tert-C_4H_9); 12,10 (1H, s NH)
V	7,68	6,59	6,45	10,04	3,42	1,20	1,30...2,20 (10H, m, cyclo$(CH_2)_5$); 4,04 (1H, m, cyclo-CH); 11,82 (1H, br.d 7,5, NH)
VII	6,87	6,17	6,40	10,15	3,35	1,18	7,20...7,50 (5H, m C_6H_5); 12,92 (1H, s NH)
VIII	7,55	6,53	6,41	9,97	3,41	1,20	1,22 (6H, t, 7,0, $N(CH_2\underline{CH_3})_2$); 3,65 (4H, q 7,0, $N(\underline{CH_2})CH_3)_2$)
IX	7,65	6,58	6,42	9,98	3,42	1,20	1,80 (6H, m, cyclo$(CH_2)_3$); 3,55 (4H, m, cyclo$N(CH_2)_2$)
XI	7,01	6,60	6,52	9,93	3,49	1,24	7,11; 7,31& 7,64 (about 1H, m $C_3H_3N_2$)
XVI	7,87	6,52	6,43	8,81	3,40	1,20	1,29 (9H, s, tert-C_4H_9-N=); 1,55 (9H, s, tert-C_4H_9-NH); 13,02 (1H, br.s, NH)
XVII	7,68	6,50	6,42	8,78	3,40	1,20	1,25...2,15 (20H, m 2-cyclo$(CH_2)_5$); 3,10 (1H, m, CH-N=); 4,05 (1H, m, CH-N); 12,80 (1H, br.m NH)
XVIII	7,78	6,41	6,50	8,91	3,40	1,20	4,60 (2H, s, CH_2N=); 4,95 (2H, d 5,0, $C\underline{H_2}NH$); 7,00...7,40 (10H, m $2C_6H_5$); 12,95 (1H, br t, 5,0, NH)
XIX	7,00	6,19	6,41	9,15	3,35	1,18	7,10...7,45 (10H, m, $2C_6H_5$); 14,17 (1H, s, NH)
XVII*	7,72	6,65	6,34	8,60	3,40	1,11	1,20...2,10 (20H, s 2-cyclo$(CH_2)_5$); 3,02 (1H, m CH-N=); 4,11 (1H, m CH-N)
XVII**	7,80	6,70	6,29	8,34	3,42	1,12	1,20...2,10 (20H, m 2cyclo$(CH_2)_5$); 3,55 (1H, m CHN=); 3,80 (1H, m CH-N)

*Spectrum taken in CD_3OD.

**With 1.2 equiv. CF_3COOH added.

TABLE 3. PMR Spectra of Coumarins (XIII)-(XV) and (XX) in $CDCl_3$

Compound	Chemical shifts, δ, ppm (coupling constant, J, Hz)					
	1-CH_2 7-CH_2 (t, 6.5)	2-CH_2 6-CH_2 (m)	3-CH_2 5-CH_2 (m)	8-H (s)	10-CH= (s)	other protons
XIII	2,87 2,25	1,95* 1,85	3,27	6,42	10,15	7,20...7,50 (5H, m, C_6H_5); 12,80 (1H, m, NH)
XIV	2,85 2,73	1,97	3,31	7,21	10,01	3,57 (4H, t, 5,0, $N(CH_2)_2$); 3,94 (4H, t, 5,0, $O(OCH_2)_2$)
XV	2,85 2,62	1,98	3,36	6,50	9,82	7,05; 7,26& 7,58 (about 1H, m $C_3H_3N_2$)
XX	2,87**	2,00	3,25	6,64	9,03	7,40...8,10 (10H, m $2C_6H_5$); 14,20 (1H, s, NH)

*Two triplet signals (J = 6.0 Hz).

**Multiplet.

It must be noted that the precise localization of the $H_{(2)}$ atom on the $N_{(2)}$ atom shows that this molecule exists in the keto-amine tautomeric form in the ground state. Transfer of the $H_{(2)}$ atom to the $O_{(2)}$ atom with the formation of an oximine group is probable on excitation of the molecule. One further feature of the structure of (XIII) is the conformational flexibility of the julolidine fragment appearing as a disorder at the $C_{(10)}$ and $C_{(13)}$ atoms. Since the experiment was carried out at −90°C this disorder is static and not dynamic in character. The conformations of these rings are different, from an intermediate between a half-chair and a chair to a twisted boat.

The ^{13}C NMR spectra (Table 4) of compounds (IV), (VI), (VII), and (XIX), and of aldehyde (X) [5] and 4-benzylamino-7-diethylaminocoumarin (XXIII) used for comparison, confirm the retention of the coumarin structure and particularly the presence of the lactone carbonyl group which does not participate in the formation of an IMHB. A strong displacement towards low field was observed for the signal for the $C_{(3)}$ atom, compared with the corresponding 3-unsubstituted coumarins, and in the spectra of the aldehydes (IV), (VI), (VII), and (X) in difference to other known 7-amino-3-formylcoumarins [5]. Comparison with the ^{13}C NMR spectrum of the coumarin (XXIII) with the coumarin (XXII) described previously [6] showed that for compounds (IV) and (VI) a significant displacement towards low field is detected for the signals of the $C_{(4)}$ and $C_{(5)}$ atoms (Δ ~ 5-10 ppm). The analogous effect was less than 3-4 ppm [5] for 7-amino-3-formylcoumarins containing H, Cl, or a CH_3 group in position 4. The indicated "nonadditive effects" [15] are evidently the result of intramolecular interaction of the substituents at positions 3 and 4. The presence of a chelate ring in the molecules (IV), (VI), and (VII) must lead to a large fixation of the substituent at the $N_{(4)}$ atom and a reduction of the electron density at the carbon atom of the formyl group. This was also confirmed by the displacement of the signal of the aldehyde carbon atom in coumarins (IV), (VI), and (VII) towards low field in comparison with coumarin (X). The ^{13}C NMR spectrum of azomethine (XIX) was very similar to the spectrum of aldehyde (VII), which confirms the identical isomeric form of both compounds.

On the basis of the available data of ^{13}C and ^1H NMR spectroscopy and the results of the X-ray structural investigation it may be concluded that aldehydes (IV)-(X), (XIII) and azomethines (XVI)-(XX) exist in the same chelate form of structure A.

In the electronic absorption spectra of coumarins (IV)-(XX) in ethanol or in acetonitrile (Table 5) the long-wave maximum underwent a bathochromic shift of 30-60 nm compared with the corresponding 4,7-diaminocoumarins [16]. This regularity was in agreement with the large charge distribution in molecules (IV)-(XX) caused by the introduction of a strong electron-accepting group at position 3. The significant bathochromic shift of the absorption maxima of azomethines (XVI)-(XVIII) on changing from alcohol to acetonitrile solution is worthy of attention. This is in contrast to the corresponding aldehydes (IV)-(VI) and the other known 7-aminocoumarins [17]. Recording the PMR spectrum of coumarin (XVII), for example, in $CDCl_3$, CD_3CN, and CD_3OD did not show a significant difference in CS for the protons of the substituents at positions 3 and 4. In addition the CS of the chelate proton was retained practically the same in CD_3CN, where there is no rapid deuterium exchange (unlike CD_3OD), as in $CDCl_3$. Consequently, the change in absorption spectra of the azomethines in acetonitrile is caused not by a change in structure of the isomers but by the solvating ability of the solvent.

The compounds studied usually possessed a weak fluorescence in the range 460-520 nm (Table 5). The exception was the aldehyde (XV), the fluorescence quantum yield of which was fairly high (Q_f 0.7). On the whole the same rules were followed in the fluorescence spectra of compounds (IV)-(XX) as in the absorption spectra. Two emission bands were success-

TABLE 4. ^{13}C NMR Spectra of Coumarins (IV), (VI), (VII), (X), (XIX), and (XXIII) in $CDCl_3$

Compound	Chemical shifts (coupling constants, $J^{13}C, ^1H$, Hz)											
	C-2 s	C-3	C-4 m	C-4a m	C-5 d	C-6 dd	C-7 m	C-8 dd	C-8a dd	7-NCH_2 t	7-NCH_2CH_3 q	other carbon items
IV	164,4	96,0 (dd 17,3; 7,4)	159,8	100,8	131,4 (158,2)	107,4 (161,2; 5,0)	152,0	98,0 (160,0; 4,9)	157,8 (8,5; 5,5)	44,8 (136,9)	12,5 (127,0)	31,3 (q 126,8); 55,1 (m); 190,8 (d) 180,7)
VI	163,9	95,0 (dd 17,3; 6,5)	159,6	101,0	129,2 (158,8)	108,2 (161,4; 6,5)	152,1	98,2 (161, 1; 4,8)	157,9 (9,6; 5,2)	44,8 (136,9)	12,4 (126,9)	50,8 (t 139,6); 127,0 (d 163,9); 128,2 (d,160,7); 129,1 (d, 161,1); 136,5 (m); 190,7 (d, 180,6)
VII	163,8	96,0 (dd 17,3; 5,3)	157,7	100,2	129,2 (162,0)	107,8 (161,6; 5,5)	152,1	97,7 (161,3; 5,1)	158,0 (9,5; 5,4)	44,8 (135,9)	12,4 (126,9)	125,8 (d, 162,0); 127,6 (d, 162,2); 129,8 (d, 162,2); 191,4 (d 181,0)
X*	160,2	101,8 (d, 23,2)	164,9	104,6	128,6 (159,1)	108,8 (161,4; 5,7)	151,6	97,6 (161,1; 5,2)	157,2	44,7 (136,3)	12,3 (127,0)	54,0 (t, 140,0); 66,9 (t, 143,7); 186,9 (d,181,5)
XIX	163,9	93,8 (d 6,3)	155,2	101,7	128,6 (161,9)	107,4 (160,6; 5,9)	151,0	97,7 (160,6; 5,1)	156,9 (9,7; 4,9)	44,6 (135,8)	12,5 (126,9)	121,0 (d, 158,8); 124,9 (d, 160,8); 125,4 (d, 161,8); 126,2 (d, 162,1); 129,2 (d, 160,4); 129,6 (d, 161,5); 141,0(m); 149,9 (m); 159,1 (d, 164,8)
XXII**	162,3	78,9 (dd 164,0; 5,9)	154,0	102,3	123,5 (158,8)	107,7 (160,4; 5,8)	150,1	96,6 (159,6; 5,5)	155,5 (9,4; 4,1)	43,7 (135,6)	12,2 (127,1)	45,2(t,137,8); 126,7 (d. 158,1); 126,9 (d, 160,1); 128,4 (d, 160,7); 134,3 m

*According to [5].

**Spectrum taken n DMSO-d_6.

TABLE 5. Spectral and Luminescent Properties of the 7-Aminocoumarins (IV), (V), (VII)-(IX), (XI), and (XIII)-(XX)

Compound	Solvent	UV spectrum, λ_{max}, nm (log ε)	Fluorescence* λ_{max}, nm
IV	C_2H_5OH	245 (4,27); 262 (3,97); 276 (3,89); 310 (3,89); 326 (3,87); 382 (4,65)	485
	CH_3CN	242 (4,20); 260 (3,95); 276 (3,83); 312 (3,85); 326 (3,83); 380 (4,64)	485
V	C_2H_5OH	245 (4,38); 360 (4,02); 275 (3,90); 310 (3,92); 325 (3,88); 377 (4,72)	466
	CH_3CN	245 (4,29); 260 (4,09); 275 (3,96); 311 (3,97); 326 (3,95); 375 (4,69)	466
VII	C_2H_5OH	239 (4,43); 278 (4,06); 303 (3,97); 311 (4,01); 388 (4,73)	460
	CH_3CN	237 (4,30); 278 (3,94); 307 (3,88); 312 (3,91); 386 (4,61)	460
VIII	C_2H_5OH	248 (4,10); 260 (4,05); 284 (3,74); 318 (3,72); 406 (4,56)	472
	CH_3CN	246 (4,03); 260 (3,95); 283 (3,55); 324 (3,75); 402 (4,13)	472
IX	C_2H_5OH	248 (4,13); 285 (3,80); 316 (3,73); 403 (4,58)	469
	CH_3CN	245 (4,06); 283 (3,67); 400 (4,57)	469
XI	C_2H_5OH	258 (4,04); 290 (3,91); 456 (4,51)	500
	CH_3CN	250 (3,27); 270 (3,81); 280 (4,83); 290 (3,75); 460 (4,62)	516
XIII	C_2H_5OH	230 (4,49); 290 (4,10); 317 (3,94); 408 (4,62)	470; 512
	CH_3CN	227 (4,49); 289 (4,07); 317 (3,91); 405 (4,49)	468; 510
XIV	C_2H_5OH	252 (4,08); 294 (3,93); 430 (4,55)	492
	CH_3CN	252 (3,99); 294 (3,87); 424 (4,55)	490
XV	C_2H_5OH	294 (3,92); 384 (3,64); 476 (4,66)	520**
	CH_3CN	260 (3,94); 290 (4,04); 289 (4,02); 469 (4,56)	518**
XVI	C_2H_5OH	264 (4,24); 271 (4,33); 304 (4,07); 325 (3,99); 366 (4,49); 379 (4,62)	480
	CH_3CN	254 (4,31); 270 (4,14); 310 (4,05); 328 (4,10); 386 (4,37); 421 (4,52)	505
XVII	C_2H_5OH	264 (4,29); 271 (4,36); 302 (4,11); 329 (3,99); 360 (4,54); 375 (4,67)	455
	CH_3CN	254 (4,29); 271 (4,01); 328 (4,05); 314 (4,01); 364 (4,22); 408 (4,52)	498
XVIII	C_2H_5OH	242 (4,38); 272 (4,49); 302 (4,27); 313 (4,19); 322 (4,15); 377 (4,75)	455
	CH_3CN	251 (4,39); 272 (4,08); 314 (4,12); 324 (4,14); 383 (4,44); 414 (4,57)	470; 490
XIX	C_2H_5OH	240 (4,33); 276 (4,14); 318 (3,93); 405 (4,64)	—
	CH_3CN	254 (4,13); 267 (4,25); 320 (3,83); 416 (4,64)	—
XX	C_2H_5OH	236 (4,56); 250 (4,58); 266 (4,43); 305 (4,25); 370 (4,60); 435 (3,91)	487
	CH_3CN	234 (4,58); 249 (4,61); 302 (4,24); 369 (4,61); 429 (3,94)	440; 510

*Relative quantum yield of fluorescence $\varphi_f < 0.10$.

**φ_f (C_2H_5OH) = 0.75; φ_f (CH_3CN) = 0.68.

fully observed for the coumarins (XVIII) and (XX) in acetonitrile. In view of this the absorption and fluorescence spectra of the coumarins (XVIII) and (XX) were studied in a more representative series of solvents: hexane, benzene, 1,4-dioxane, acetone, and DMF. It was discovered as a result that two emission bands were observed in the majority of the solvents listed. However, according to the PMR spectra obtained in C_6D_6, in which both coumarins have a double fluorescence, the indicated compounds exist in the ground state as a single isomeric form. The possibility of the appearance of double fluorescence for the azomethines (XIII), (XVI)-(XX) may be linked with the generation of a TICT state or with proton transfer on photoexcitation. This requires special study and will be the subject of a separate communication.

EXPERIMENTAL

The IR spectra were taken on a Perkin–Elmer 577 spectrophotometer. The UV spectra and fluorescence spectra were taken on a Hitachi EPS-3T spectrophotometer fitted with a G-3 fluorescence attachment. Fluorescence quantum yields (φ_f) were determined relative to 3-aminophthalimide by the procedure of [19]. The ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument, internal standard was HMDS.

TABLE 6. Coordinates of Atoms ($\times 10^4$, and $\times 10^3$ for H atoms) in the Compound (XIII) Molecule

Atom	x	y	z	Atom	x	y	z
$O_{(0)}$	1621(2)	1253(1)	-95(2)	$C_{(19)}$	1216(3)	-4068(2)	-592(3)
$O_{(1)}$	3101(2)	368(1)	821(2)	$C_{(20)}$	818(3)	-3497(2)	178(3)
$C_{(2)}$	2082(3)	545(2)	-47(2)	$C_{(21)}$	965(3)	-2660(2)	-25(2)
$C_{(3)}$	1634(3)	-122(2)	-768(2)	$H_{(2)}$	100(4)	-137(2)	-180(3)
$C_{(4)}$	2204(3)	-928(2)	-592(2)	$H_{(2)}$	409(3)	-225(2)	-5(2)
$C_{(4a)}$	3373(3)	-1060(2)	258(2)	$H_{(9.1)}$	529(5)	71(3)	221(3)
$C_{(5)}$	4240(3)	-1789(2)	430(2)	$H_{(9.2)}$	405(5)	48(2)	283(3)
$C_{(6)}$	5320(3)	-1885(2)	1271(2)	$H_{(10.0)}$	606(4)	45(2)	413(3)
$C_{(7)}$	5575(3)	-1221(3)	2024(2)	$H_{(10.1)}$*	490(6)	-57(3)	415(4)
$C_{(8)}$	4806(3)	-466(2)	1840(2)	$H_{(10a)}$*	733(9)	37(4)	290(6)
$C_{(8a)}$	3763(3)	-402(2)	956(2)	$H_{(11.1)}$	722(3)	-88(2)	434(2)
$N_{(1)}$	6575(3)	-1324(1)	2914(2)	$H_{(11.2)}$	788(11)	-31(6)	343(7)
$C_{(9)}$	5060(4)	251(2)	2610(3)	$H_{(12.1)}$	803(3)	-205(2)	372(3)
$C_{(10)}$*	5608(10)	-86(5)	3757(7)	$H_{(12.2)}$	641(8)	-250(4)	363(6)
$C_{(10a)}$*	6356(10)	144(5)	3405(6)	$H_{(13.0)}$	789(4)	-319(2)	247(3)
$C_{(11)}$	6681(6)	-695(3)	3751(3)	$H_{(13.1)}$**	854(6)	-219(6)	198(4)
$C_{(12)}$	7348(6)	-2102(2)	3115(4)	$H_{(13a)}$***	585(13)	-306(6)	282(9)
$C_{(13)}$**	7595(7)	-2590(4)	2172(5)	$H_{(14.1)}$	661(6)	-282(3)	78(4)
$C_{(13a)}$***	6817(15)	-2838(7)	2578(10)	$H_{(14.2)}$	555(5)	-313(3)	141(3)
$C_{(14)}$	6229(4)	-2674(2)	1402(3)	$H_{(15)}$	17(3)	68(2)	-161(2)
$C_{(15)}$	500(3)	73(2)	-1612(3)	$H_{(17)}$	230(3)	-278(2)	-242(2)
$O_{(2)}$	-47(2)	-413(1)	-2314(2)	$H_{(18)}$	204(4)	-417(2)	-204(3)
$N_{(2)}$	1638(3)	-1539(1)	-1243(2)	$H_{(19)}$	113(3)	-466(2)	-47(2)
$C_{(16)}$	1541(3)	-2400(2)	-966(2)	$H_{(20)}$	42(3)	-364(2)	81(2)
$C_{(17)}$	1951(3)	-2974(2)	-1765(2)	$H_{(21)}$	65(3)	-226(2)	46(2)
$C_{(18)}$	1782(3)	-3804(2)	-1561(3)				

*Position occupancy factor 0.5.

**Position occupancy factor 0.7.

***Position frequency factor 0.3.

The physicochemical characteristics of the coumarins obtained are given in Tables 1-6. The data of elemental analysis for C, H, and N for compounds (IV)-(XX) corresponded with calculated values.

General Method of Synthesis of Coumarins (IV)-(XX) from 7-Amino-4-chloro-3-formylcoumarins (I)-(III). The appropriate amine (10-40 mmole) was added to a solution of the initial 7-amino-4-chloro-3-formylcoumarin (I)-(III) (4 mmole) in absolute benzene (20 ml) or 1,4-dioxan. The quantity of primary amine must not exceed 8-10 mmole in the synthesis of the formyl derivatives (IV)-(VII) and (XIII) but it must be raised to 20-40 mmole to obtain the azomethines (XVII)-(XX). The reaction mixture was stirred for 2-4 h at 20-60°C, the solid formed was filtered off, and the filtrate evaporated in vacuum. The residue was chromatographed on a column (20 × 2 cm) of silica gel Silpearl UV-254, eluent was hexane–acetone varying from 10:1 to 3:1. The chromatographically pure product was crystallized from hexane–acetone where necessary.

General Method of Synthesis of Coumarins (IV)-(VI) and (VIII)-(X) from 4,7-Diaminocoumarins (XXI)-(XXVI). A solution of 4,7-diaminocoumarin (XXI)-(XXVI) (4 mmole) in absolute DMF (20-40 ml) was added to the Vilsmeier complex obtained by stirring absolute DMF (6-10 mmole) and the equivalent quantity of freshly distilled $POCl_3$ for 1 h at 20°C. The reaction mixture was stirred for 2-6 h at 20-60°C until disappearance of the initial coumarin (checked by TLC). The solution was poured into ice water (400 ml), and left overnight at 5°C. The precipitated solid was filtered off, washed with water, and dried at a temperature below 70°C. The product was crystallized from hexane–acetone.

X-Ray Structural Investigation of Coumarin (XIII). Crystals of compound (XIII) were rotated with slow evaporation of solution in a hexane–acetone mixture. The unit cell parameters and the experimental set of intensities for the coumarin (XIII) were measured on a Siemens 4-circle diffractometer P3/PC (λ MoK_α, graphite monochromator, $\Theta/2\Theta$ scanning mode to $\Theta \leq 28°$) at −90°C.

TABLE 7. Valence Angles in Compound (XIII)

Angle	ω, deg	Angle	ω, deg
$C_{(2)}O_{(1)}C_{(8a)}$	121,8(2)	$C_{(4a)}C_{(8a)}C_{(8)}$	123,6(2)
$OC_{(2)}O_{(1)}$	115,4(2)	$C_{(7)}N_{(1)}C_{(11)}$	119,7(3)
$OC_{(2)}C_{(3)}$	127,1(3)	$C_{(7)}N_{(1)}C_{(12)}$	120,8(3)
$O_{(1)}C_{(2)}C_{(3)}$	117,4(2)	$C_{(11)}N_{(1)}C_{(12)}$	118,8(3)
$C_{(2)}C_{(3)}C_{(4)}$	121,4(2)	$C_{(8)}C_{(9)}C_{(10)}$	109,0(4)
$C_{(2)}C_{(3)}C_{(15)}$	115,8(2)	$C_{(8)}C_{(9)}C_{(10a)}$	114,3(4)
$C_{(4)}C_{(3)}C_{(15)}$	122,7(2)	$C_{(9)}C_{(10)}C_{(11)}$	115,2(6)
$C_{(3)}C_{(4)}C_{(4a)}$	118,7(2)	$C_{(9)}C_{(10a)}C_{(11)}$	116,0(6)
$C_{(3)}C_{(4)}N_{(2)}$	118,4(2)	$N_{(1)}C_{(11)}C_{(10)}$	119,9(5)
$C_{(4a)}C_{(4)}N_{(2)}$	122,9(2)	$N_{(1)}C_{(11)}C_{(10a)}$	116,6(4)
$C_{(4)}C_{(4a)}C_{(5)}$	125,8(2)	$N_{(1)}C_{(12)}C_{(13)}$	115,6(4)
$C_{(4)}C_{(4a)}C_{(8a)}$	118,2(2)	$N_{(1)}C_{(12)}C_{(13a)}$	121,1(6)
$C_{(5)}C_{(4a)}C_{(8a)}$	115,9(2)	$C_{(12)}C_{(13)}C_{(14)}$	115,0(5)
$C_{(4a)}C_{(5)}C_{(6)}$	123,2(2)	$C_{(12)}C_{(13a)}C_{(14)}$	112,1(7)
$C_{(5)}C_{(6)}C_{(7)}$	118,8(2)	$C_{(6)}C_{(14)}C_{(13)}$	112,6(3)
$C_{(5)}C_{(6)}C_{(14)}$	120,7(3)	$C_{(6)}C_{(14)}C_{(13a)}$	113,2(5)
$C_{(7)}C_{(6)}C_{(14)}$	120,5(2)	$C_{(3)}C_{(15)}O_{(2)}$	126,0(3)
$C_{(6)}C_{(7)}C_{(8)}$	119,7(2)	$C_{(4)}N_{(2)}C_{(16)}$	127,8(2)
$C_{(6)}C_{(7)}N_{(1)}$	119,7(2)	$N_{(2)}C_{(16)}C_{(17)}$	119,4(2)
$C_{(8)}C_{(7)}N_{(1)}$	120,6(2)	$N_{(2)}C_{(16)}C_{(21)}$	120,5(2)
$C_{(7)}C_{(8)}C_{(8a)}$	118,5(2)	$C_{(17)}C_{(16)}C_{(21)}$	120,0(3)
$C_{(7)}C_{(8)}C_{(9)}$	121,2(2)	$C_{(16)}C_{(17)}C_{(18)}$	119,9(3)
$C_{(8a)}C_{(8)}C_{(9)}$	120,3(2)	$C_{(17)}C_{(18)}C_{(19)}$	120,4(3)
$O_{(1)}C_{(8a)}C_{(4a)}$	122,0(2)	$C_{(18)}C_{(19)}C_{(20)}$	119,7(3)
$O_{(1)}C_{(8a)}C_{(8)}$	114,4(2)	$C_{(19)}C_{(2)}C_{(21)}$	120,3(3)
		$C_{(16)}C_{(21)}C_{(20)}$	119,6(3)

The bright yellow crystals of (XIII) were monoclinic: a = 8.641(2), b = 16.213(3), c = 12.296(2) Å; β = 92.93(3)°, V = 1720(1) Å^3, M = 360, d_{calc} = 1.39 g/cm^3, Z = 4, $C_{22}H_{20}N_2O_3$, space group P $2_{1/c}$.

The structure was solved by the first method and refined by the method of least squares in an isotropic and then in an anisotropic approach. The disorder of atoms $C_{(10)}$ and $C_{(13)}$ at two positions (see above) was allowed for in this way. In the first case the positions have equal occupancy of 0.5 and in the second 0.7 and 0.3 for positions $C_{(13)}$ and $C_{(13a)}$, respectively. All the hydrogen atoms were made apparent by generating difference series and were refined isotropically. This included the H atoms bound to the disordered C atoms. The $H_{(10.0)}$ atom is bound simultaneously both with atom $C_{(10)}$ and with atom $C_{(10a)}$, and atom $H_{(13.0)}$ with atoms $C_{(13)}$ and $C_{(13a)}$. These hydrogen atoms were refined with a position occupancy factor equal to one. The final value of the agreement factor R was 0.036 (wR = 0.036) for 1521 reflections with $F^2 > 3\sigma$.

All calculations were carried out using the SHELXTL-PC program package on an IBM/AT computer. Atomic coordinates are given in Table 6, valence angles are given in Table 7.

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