2-Chloro-3,4-dihydroimidazole. Part 2.[1] Synthesis of Cyanines from 6-Aryl-2,3-dihydro-6aH-imidazo[1,2-a]pyrido[1,2-c][1.3.5]triazin-5(6H)-ones. Crystal and Molecular Structure of 6-Phenyl-2,3-dihydro-6aH-imidazo[1,2-a]pyrido[1,2-c]-[1,3,5]triazin-5(6H)-one

Franciszek Sączewski *
Department of Organic Chemistry, Medical Academy, 80-416 Gdańsk, Poland
Maria Gdaniec
Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland
Krzysztof Ośmiałowski
Department of Inorganic Chemistry, Medical Academy, 80-416, Gdańsk, Poland

2-Chloro-3,4-dihydroimidazole (1) reacts with pyridine and aromatic isocyanates to give 6-aryl-2,3-dihydro-6aH-imidazo[1.2-a]pyrido[1,2-c][1,3,5]triazin-5(6H)-ones (5a—g). The crystal and molecular structure of 6-phenyl-2,3-dihydro-6aH-imidazo[1,2-a]pyrido[1,2-c][1,3,5]triazin-5(6H)-one (5a) determined from X-ray diffraction data is presented. Reaction of the compounds (5a—f) with malononitrile provides a new route to the cyanines (8a—f).

Nucleophilic ring-opening reactions of quaternary pyridinium salts[2] or pyridinium salts bearing cationic substituents[3] with compounds containing active methylene groups in the presence of a base such as hydroxide or amine are well known methods of synthesizing polymethine dyes. Earlier[4] we described the reaction of 2-chloro-3,4-dihydroimidazole (1) with pyridine or isoquinoline to give the cyclic biguanide analogues (2) and (3). The intermediate pyridinium salt (4) was too unstable to be isolated. We have now found that the latter can be trapped by aromatic isocyanates to give the adducts (5a—g) which, in turn, provide access to the cyanines (8a—f).
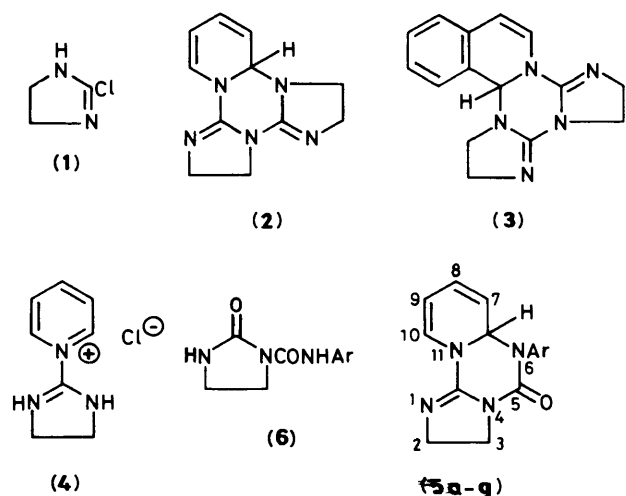
Results and Discussion

Treatment of compound (1) with pyridine in the presence of aryl isocyanates in CH_2Cl_2 at 0 °C afforded 6-aryl-2,3-dihydro-6aH-imidazo[1,2-a]pyrido[1,2-c][1,3,5]triazine-5(6H)-one hydrochlorides which with cold aqueous sodium carbonate were converted into a more stable bases (5a—g). These products were found to be very unstable in acid solution and readily decomposed to N-arylaminocarbonylimidazolidinones (6) when treated with 10% HCl at 20 °C. The structure of the dihydropyridines (5a—g) was confirmed by i.r., [1]H n.m.r., and by X-ray analysis of (5a).

Although it was expected that the reaction of (1) with pyridine homologues would proceed similarly, isoquinoline in place of pyridine gave compound (3), and the reaction with pyridine in the presence of less active isothiocyanates or aliphatic isocyanates led to the formation of (2).
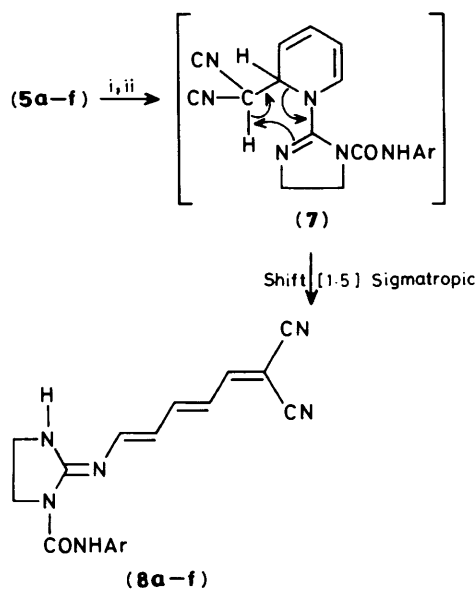
Treatment of the dihydropyridines (5a—f) with malononitrile in solvents such as a CH_2Cl_2, MeCN, or EtOH gave rise to the red cyanines (8a—f). A reasonable reaction path (Scheme 1) involves formation of the intermediate (7) followed by a [1,5] sigmatropic shift of the hydrogen atom and rearrangement to

(5a—f) →[i,ii] (7)

Shift [1·5] Sigmatropic

(8a—f)

a; Ar = Ph
b; Ar = C_6H_4OMe—m
c; Ar = C_6H_4OMe—p
d; Ar = C_6H_4Cl—m
e; Ar = C_6H_4Cl—p
f; Ar = C_6H_4CF$_3$—m

Scheme 1. *Reagents:* i, MeCN; ii, $CH_2(CN)_2$

(1)

(2)

(3)

(4)

(6)

(5a—g)

a; Ar = Ph
b; Ar = C_6H_4OMe—m
c; Ar = C_6H_4OMe—p
d; Ar = C_6H_4Cl—m
e; Ar = C_6H_4Cl—p
f; Ar = C_6H_4CF$_3$—m
g; Ar = 1—Naphthyl

the more stable all-*trans* isomers. Since ^{1}H n.m.r. spectral results failed to establish the all-*trans* configuration of compounds (**8a—f**) because of overlap in the aromatic proton signals and we were unable to obtain crystals suitable for X-ray analysis, compound (**8a**) was prepared independently by an alternative method. Thus a simple ring opening of the pyridinium salt (**4**) with malononitrile and pyridine gave (**9**)·HCl the all-*trans* configuration of which follows from the $^3J_{HH}$ coupling constants, which differ by less than 1.5 Hz. The reaction of (**9**) with phenyl isocyanate in pyridine produced compound (**8a**) identical with that obtained from the reaction of (**5a**) with malononitrile (Scheme 2).
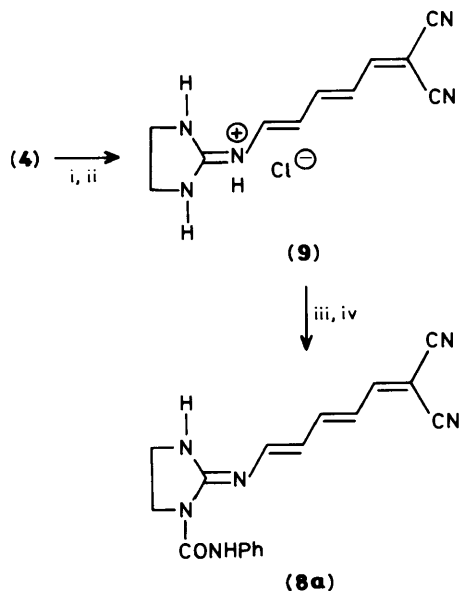
Scheme 2. *Reagents:* i, CH$_2$Cl$_2$; ii, CH$_2$(CN)$_2$, pyridine; iii, PhNCO, pyridine; iv, light petroleum

It is noteworthy, that dihydropyridines (**5**) react readily with enolizable active methylene compounds such as Meldrum's acid of dimedone. In these cases, however, mixtures of the unstable products were formed.

Crystal Data for the Compound (**5a**).—C$_{15}$H$_{14}$N$_4$O, M = 266.3, Monoclinic, a = 5.969 7(6), b = 12.259 7(8), c = 17.981(2) Å, V = 1 313.8(2) Å^3, Z = 4, D_c = 1.3 g cm^{-3}, $F(000)$ = 560, μ(Cu-K_α) = 6.31 cm^{-1}. Single crystals of (**5a**) were obtained by recrystallization from ethanol and the lattice parameters were determined by a least-squares fitting of the setting angles of 15 reflections. A crystal of dimensions 0.15 × 0.2 × 0.2 mm was used for the measurement of Bragg intensities on a Syntex $P2_1$ diffractometer with graphite monochromatized Cu-K_α radiation (λ = 1.542 78 Å) in the 2θ range 5—115°. Out of 2 024 measured reflections, 1 437 had $I \geqslant 1.96\sigma(I)$ and were considered observed. Lorentz and polarization corrections were applied but absorption corrections were ignored.

Structure solution. The structure was assigned by direct methods with MULTAN80[5] and refined by the full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms (H atoms located on a ΔF map). Empirical isotropic extinction parameter x was used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$; x converted at 0.019(2). Final values of R and R_w are 0.040 and 0.055, respectively. The weights were w = 1/[$\sigma^2(F_o)$ + 0.0002F_o^2]. The residual intensity in the final difference map was in a range ±0.15 e Å^{-3}. Calculations were performed using the programs SHELX76[6]
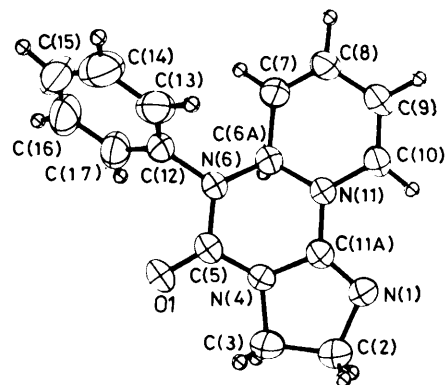
Figure 1. ORTEP plot of the molecule (**5a**) showing the numbering scheme
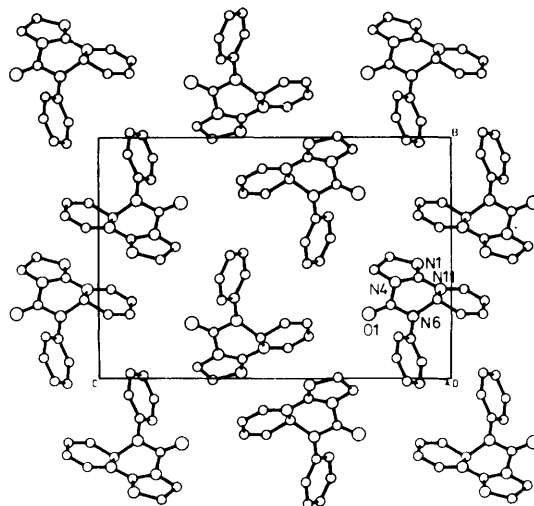
Figure 2. The crystal structure viewed down the *a* axis

for scattering factors and structure refinement PLUTO[7] and ORTEP[8] for drawings, and programs written by Jaskólski[9] for molecular geometry analysis.

The final atomic parameters are presented in Table 2. The lists of isotropic and anisotropic thermal parameters of nonhydrogen atoms and parameters of H atoms are available on request from the Cambridge Crystallographic Data Centre.*

A drawing of the molecule with its numbering scheme is shown in Figure 1. Bond distances, valence angles, and important torsion angles are given in Table 3.

The three triazine nitrogen atoms show different degrees of pyramidality. The extent to which the sum of the bond angles around an atom (Σv) differs from 360°, as well as the distance d of an atom from the plane defined by the atoms connected to it provide a measure of the planarity of the atom. Table 4 gives both these values for the triazine nitrogen atoms.

There is only one N–C double bond of length 1.267(3) Å in the molecule, several C(sp^2)–N bonds with lengths in the range 1.369(3)—1.433(3) Å and four C(sp^3)–N single bonds with lengths in the range 1.463(3)—1.491(3) Å. The longest of C(sp^2)–N bonds is N(6)–C(12). The plane through the phenyl ring and the plane through N(6), C(6A), and C(5) form a dihedral angle of 74° and therefore there is no π-type

---

Table 1. Analytical data for compounds (**5a**—**g**) and (**8a**—**f**)

Compound formulae (M)	Found (%) (required) C	H	N	Yield (%)	M.p. (°C)†	$v_{max.}$(KBr) cm^{-1}	δ (a) (CDCl$_3$) (b) [(CD$_3$)$_2$SO] (p.p.m.)	m/z (relative intensity)	$\lambda_{max.}$/nm (EtOH) (log ε)
(**5a**) C$_{15}$H$_{14}$N$_4$O (266.3)	67.7 (67.6)	5.5 (5.3)	20.7 (21.0)	65	189—191	3 080, 2 885, 1 685, 1 650, 1 585, 1 490, 1 460, 1 380, 1 325, 760	(a) 3.9 (m, 4 H, CH$_2$), 4.9 (dd, 7-H), 5.1 (t, 9-H), 6.0 (m, 8-H), 6.5 (dd, 6a-H), 6.9 (d, 10-H), 7.0—7.55 (m, 5 H, ArH)	266 (25, M$^+$), 147 (100), 119 (6), 93 (35), 68 (5.8)	
(**5b**) C$_{16}$H$_{16}$N$_4$O$_2$ (296.3)	64.3 (64.8)	5.1 (5.4)	18.7 (18.9)	41	173—175	3 075, 2 880, 1 685, 1 650, 1 580, 1 480, 1 375, 1 330, 1 280, 1 040, 770	(a) 3.75 (s, 3 H, OCH$_3$), 3.9 (m, 4 H, CH$_2$), 4.9 (m, 7-H), 5.1 (t, 9-H), 6.0 (m, 8-H), 6.45 (dd, 6a-H), 6.7—7.1 (m, 4 H, 10-H, ArH), 7.25 (t, 1 H, ArH)		
(**5c**) C$_{16}$H$_{16}$N$_4$O$_2$ (296.3)	65.1 (64.8)	5.1 (5.4)	18.6 (18.9)	47	181—182	3 075, 2 880, 1 685, 1 640, 1 585, 1 505, 1 375, 1 240, 1 010, 775	(a) 3.7 (s, 3 H, OCH$_3$), 3.9 (m, 4 H, CH$_2$), 4.8 (dd, 7-H), 5.05 (t, 9-H), 5.9 (m, 8-H), 6.35 (dd, 6a-H), 6.75 (d, 10-H), 6.8—7.2 (m, 4 H, ArH)		
(**5d**) C$_{15}$H$_{13}$ClN$_4$O (300.7)	60.3 (59.9)	4.0 (4.3)	18.3 (18.6)	55	165—167	3 070, 2 880, 1 680, 1 649, 1 585, 1 475, 1 425, 1 285, 765	(a) 3.9 (m, 4 H, CH$_2$), 4.8 (dd, 7-H), 5.1 (t, 9-H), 5.95 (m, 8-H), 6.4 (dd, 6a-H), 6.8 (d, 10-H), 6.95—7.3 (m, 4 H, ArH)		
(**5e**) C$_{15}$H$_{13}$ClN$_4$O (300.7)	59.8 (59.9)	4.5 (4.3)	18.8 (18.6)	58	183—184	3 090, 2 875, 1 680, 1 640, 1 580, 1 480, 1 440, 1 370, 1 275, 1 085, 800	(a) 4.0 (m, 4 H, CH$_2$), 5.0 (dd, 7-H), 5.15 (t, 9-H), 6.0 (m, 8-H), 6.5 (dd, 6a-H), 6.9 (d, 10-H), 6.95—7.6 (m, 4 H, ArH)		
(**5f**) C$_{16}$H$_{13}$F$_3$N$_4$O (334.3)	57.1 (57.4)	3.8 (3.9)	16.8 (16.7)	63	174—176	3 050, 2 860, 1 670, 1 635, 1 575, 1 440, 1 310, 1 375, 1 110	(a) 3.95 (m, 4 H, CH$_2$), 4.8 (dd, 7-H), 5.2 (t, 9-H), 6.05 (m, 8-H), 6.5 (dd, 6a-H), 6.9 (d, 10-H), 7.1—7.6 (m, 4 H, ArH)		
(**5g**) C$_{19}$H$_{16}$N$_4$O (316.3)	71.7 (72.1)	5.2 (5.0)	17.4 (17.7)	34	103—105	3 060, 2 890, 1 685, 1 640, 1 585, 1 475, 1 380, 1 295, 775	(a) 3.9 (m, 4 H, CH$_2$), 4.6 (m, 7-H), 5.1 (t, 9-H), 5.75 (m, 8-H), 6.5—7.05 (m, 2 H), 7.15—8.0 (m, 7 H, ArH)	316 (22, M$^+$), 169 (38), 147 (100), 93 (37), 79 (6.3), 68 (7.0)	
(**8a**) C$_{18}$H$_{16}$N$_6$O (332.3)	64.7 (65.0)	4.4 (4.8)	25.5 (25.2)	92	179—181	3 320, 2 910, 2 220, 1 685, 1 605, 1 575, 1 530, 1 525, 1 285, 1 230, 990	(b) 3.5—4.6 (m, 4 H, CH$_2$), 6.4—7.05 (m, 2 H), 7.2—7.95 (m, 7 H), 8.2 (d, 1 H), 9.0 (br s, NH)	213 (9, M$^+$ − PhNCO), 138 (10), 121 (26), 119 (100), 104 (14), 93 (12), 92 (17), 90 (52), 66 (41), 64 (38)	466 (4.42)
(**8b**) C$_{19}$H$_{18}$N$_6$O$_2$ (362.4)	62.6 (62.9)	4.6 (5.0)	23.0 (23.2)	91	166—169	3 340, 2 950, 2 215, 1 685, 1 615, 1 595, 1 420, 1 295, 1 240, 990	(b) 3.5—4.2 (m, 4 H, CH$_2$), 3.75 (s, 3 H, OCH$_3$), 6.3—7.1 (m, 3 H), 7.15—7.7 (m, 4 H), 7.9 (d, 1 H), 8.2 (d, 1 H), 9.0 (br s, NH)		466 (4.58)
(**8c**) C$_{19}$H$_{18}$N$_6$O$_2$ (362.4)	63.4 (62.9)	4.8 (5.0)	23.5 (23.2)	84	132—136	3 300, 2 890, 2 215, 1 680, 1 610, 1 505, 1 480, 1 425, 1 290, 1 230	(b) 3.3—4.2 (m, 4 H, CH$_2$), 3.7 (s, 3 H, OCH$_3$), 6.3 (t, 1 H), 6.6—7.1 (m, 3 H), 7.2—7.6 (m, 3 H), 7.9 (m, 2 H), 9.1 (br s, NH)		464 (4.42)

Table 1 (continued)

Compound formulae (M)	Found (%) (required)			Yield (%)	M.p. (°C)	$v_{max.}$(KBr) cm^{-1}	δ (a) (CDCl$_3$) (b) [(CD$_3$)$_2$SO] (p.p.m.) m/z (relative intensity)	$\lambda_{max.}$/nm (EtOH) (log ε)
	C	H	N					
(8d) C$_{18}$H$_{15}$ClN$_6$O (367.2)	58.3 (58.8)	4.4 (4.1)	23.1 (22.8)	86	176—179	3 370, 2 920, 2 220, 1 700, 1 630, 1 555, 1 480, 1 290, 1 240	(b) 3.4—4.2 (m, 4 H, CH$_2$), 6.1—6.7 (m, 2 H), 6.9—7.55 (m, 5 H), 7.65—8.1 (m, 2 H), 9.0 (br s, NH)	464 (4.92)
(8e) C$_{18}$H$_{15}$ClN$_6$O (367.2)	59.1 (58.8)	3.8 (4.1)	22.7 (22.8)	92	149—152	3 340, 2 910, 2 205, 1 685, 1 610, 1 540, 1 500, 1 475, 1 425, 1 280, 1 170	3.4—4.3 (m, 4 H, CH$_2$), 6.2—7.0 (m, 2 H), 7.2—7.95 (m, 6 H), 8.1 (d, 1 H), 9.0 (br s, NH)	465 (4.62)
(8f) C$_{19}$H$_{15}$F$_3$N$_6$O (400.4)	60.4 (56.9)	3.9 (3.7)	21.1 (20.9)	88	174—176	3 330, 2 910, 2 220, 1 690, 1 615, 1 510, 1 480, 1 415, 1 220, 1 110	3.45—4.5 (m, 4 H, CH$_2$), 6.25—6.9 (m, 2 H), 7.0—8.15 (m, 7 H), 8.9 (br s, NH)	464 (4.56)

† All compounds except (8c) melt with decomposition.

Table 2. Final fractional co-ordinates

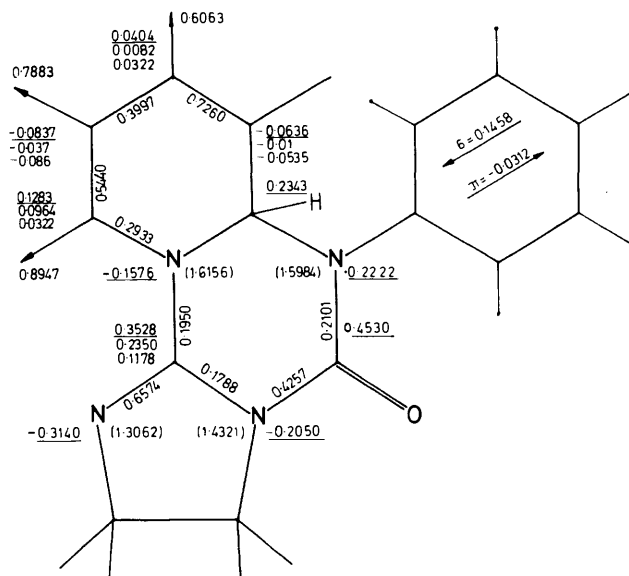| Atom	x	y	z
N(6)	1 146 3(3)	0.259 0(2)	0.109 63(9)
N(11)	0.906 6(3)	0.370 5(1)	0.031 93(9)
N(4)	0.951 6(3)	0.399 5(2)	0.160 30(9)
N(1)	0.648 1(3)	0.474 6(2)	0.097 2(1)
O(1)	1.114 1(4)	0.269 1(2)	0.235 42(9)
C(6A)	1.135 7(4)	0.328 3(2)	0.041 4(1)
C(11A)	0.824 4(4)	0.417 9(2)	0.093 8(1)
C(5)	1.076 3(4)	0.305 8(2)	0.173 4(1)
C(3)	0.828 5(6)	0.451 7(3)	0.219 8(2)
C(2)	0.631 7(5)	0.504 6(3)	0.176 4(1)
C(10)	0.782 3(4)	0.370 8(2)	−0.035 6(1)
C(9)	0.859 6(5)	0.322 8(2)	−0.094 9(1)
C(8)	1.072 9(5)	0.268 8(2)	−0.089 6(1)
C(7)	1.199 2(5)	0.268 6(2)	−0.026 5(1)
C(12)	1.289 6(4)	0.165 2(2)	0.115 6(1)
C(13)	1.216 4(5)	0.067 7(2)	0.085 0(1)
C(14)	1.358 9(9)	−0.022 1(3)	0.090 8(2)
C(15)	1.568(1)	−0.011 6(4)	0.127 2(2)
C(16)	1.636 3(6)	0.085 5(4)	0.156 7(2)
C(17)	1 498 8(5)	0.173 9(3)	0.151 1(2)

Figure 3. Molecular diagram of the molecule (5a). On selected atoms are given subsequently: excess charges (e) (underlined), excess charge populations σ and π. Electron populations of lone pairs at nitrogens are denoted in parentheses. Bond orders and free valences are also given

conjugation for this bond. The other C(sp^2)–N bonds have some double-bond character, the bond distances being independent of the degree of pyramidality of the nitrogen atoms.

The central triazine ring is severely buckled. The dihydropyridine ring has the conformation of a flattened sofa C(6A) lies 0.125(2) Å from the best plane through the other ring atoms.

The dihydroimidazole ring is nearly planar with C(3) 0.054(4) Å from the best plane through C(2), N(1), C(11A), N(4). Crystal packing viewed down the a axis is shown in Figure 2. There is a short intermolecular contact between C(10) and N(1^i) which according to its parameters: C(10) ⋯ N(1^i) 3.330(3) Å, H(10) ⋯ N(1^i) 2.49(3) Å, C(10)–H(10) ⋯ N(1^i) 148(2)° where i: 1 − x, 1 − y, − z can be termed a C–H ⋯ N bond. Utilizing these links the molecules are H-bonded to form dimers across the centre of symmetry. There are no other notable short intermolecular contacts.

Quantum chemical calculations were performed in order to calculate the charge distribution in (5a). The CNDO/2 method[10] was applied using a commercially available

program[11] adopted for the RIAD system computers. A molecular diagram of (5a) is given in Figure 3.

Experimental

M.p.s are uncorrected. The mass spectra were recorded on a LKB 9000 spectrometer, the i.r. spectra on a Specord 75 IR spectrophotometer, and the ^{1}H n.m.r. spectra on a BS-487 Tesla Brno spectrometer at 80 Hz.

Preparation of 6-Aryl-2,3-dihydro-6aH-imidazo[1,2-a]pyrido[1,2-c][1,3,5]triazin-5(6H)-ones (5a—g).—A solution of compound (1)[12] (2.5 g, 25 mmol) in CH$_2$Cl$_2$ (25 ml) was added with stirring during 0.5 h to a mixture of pyridine (6 ml) and the aromatic isocyanate (30 mmol) at 0 °C. The resulting hydrochloride (5) was separated by suction, washed with CH$_2$Cl$_2$ and Et$_2$O, and dissolved immediately in cold water

Table 3. Geometry of the molecule

(a) Bond lengths (Å)

N(1)–C(2)	1.478(3)	C(6A)–C(7)	1.491(3)
N(1)–C(11A)	1.267(3)	C(7)–C(8)	1.325(3)
C(2)–C(3)	1.519(4)	C(8)–C(9)	1.433(4)
C(3)–N(4)	1.478(3)	C(9)–C(10)	1.325(3)
N(4)–C(11A)	1.397(3)	C(10)–N(11)	1.387(3)
N(4)–C(5)	1.381(3)	N(11)–C(11A)	1.371(3)
C(5)–O(1)	1.212(3)	C(12)–C(13)	1.377(3)
C(5)–N(6)	1.369(3)	C(13)–C(14)	1.391(5)
N(6)–C(12)	1.433(3)	C(14)–C(15)	1.380(6)
N(6)–C(6A)	1.491(3)	C(15)–C(16)	1.356(6)
C(6A)–N(11)	1.463(3)	C(16)–C(17)	1.360(5)

(b) Bond angles (°)

C(2)–N(1)–C(11A)	106.5(2)	C(8)–C(9)–C(10)	120.0(2)
N(1)–C(2)–C(3)	107.3(2)	C(9)–C(10)–N(11)	120.7(2)
C(2)–C(3)–N(4)	102.4(2)	C(10)–N(11)–C(6A)	120.7(2)
C(3)–N(4)–C(11A)	106.4(2)	C(10)–N(11)–C(11A)	123.6(2)
C(3)–N(4)–C(5)	121.5(2)	C(6A)–N(11)–C(11A)	115.6(2)
C(5)–N(4)–C(11A)	122.7(2)	N(11)–C(11A)–N(1)	127.6(2)
N(4)–C(5)–N(6)	113.2(2)	N(11)–C(11A)–N(4)	115.1(2)
N(4)–C(5)–O(1)	122.4(2)	N(1)–C(11A)–N(4)	117.3(2)
O(1)–C(5)–N(6)	124.4(2)	N(6)–C(12)–C(13)	119.5(2)
C(5)–N(6)–C(6A)	116.7(2)	N(6)–C(12)–C(17)	119.7(2)
C(5)–N(6)–C(12)	118.9(2)	C(13)–C(12)–C(17)	120.8(2)
C(6A)–N(6)–C(12)	121.0(2)	C(12)–C(13)–C(14)	118.6(3)
N(6)–C(6A)–N(11)	107.0(2)	C(13)–C(14)–C(15)	119.6(4)
N(6)–C(6A)–C(7)	113.1(2)	C(14)–C(15)–C(16)	120.8(4)
N(11)–C(6A)–C(7)	111.0(2)	C(15)–C(16)–C(17)	120.2(4)
C(6A)–C(7)–C(8)	122.7(2)	C(16)–C(17)–C(12)	120.1(3)
C(7)–C(8)–C(9)	121.2(2)		

(c) Relevant torsion angles (°)

N(4)–C(5)–N(6)–C(6A)	16.4(2)
C(5)–N(6)–C(6A)–N(11)	−53.3(3)
N(6)–C(6A)–N(11)–C(11A)	50.2(2)
C(6A)–N(11)–C(11A)–N(4)	−12.5(2)
N(11)–C(11A)–N(4)–C(5)	−30.2(2)
C(11A)–N(4)–C(5)–N(6)	27.6(2)
N(11)–C(6A)–C(7)–C(8)	8.8(3)
C(6A)–C(7)–C(8)–C(9)	−3.2(3)
C(7)–C(8)–C(9)–C(10)	−2.1(3)
C(8)–C(9)–C(10)–N(11)	0.6(3)
C(9)–C(10)–N(11)–C(6A)	6.3(2)
C(10)–N(11)–C(6A)–C(7)	−10.4(2)
N(1)–C(2)–C(3)–N(4)	3.1(3)
C(2)–C(3)–N(4)–C(11A)	−3.2(3)
C(3)–N(4)–C(11A)–N(1)	2.5(3)
N(4)–C(11A)–N(1)–C(2)	−0.4(2)
C(11A)–N(1)–C(2)–C(3)	−1.8(3)

Table 4. Σv and d for tertiary triazine N atoms

	Σv	d (Å)
N(4)	350.5	0.252(2)
N(6)	356.6	0.152(2)
N(11)	359.9	0.032(2)

(30—250 ml). This solution was filtered into cold aqueous Na_2CO_3 (10%) to give free base (5) which was filtered off and recrystallized from EtOH or EtOH–H_2O. Analytical data for compounds (5a—g) are given in Table 1.

Preparation of 6-(1-Arylaminocarbonyl-2,3,4,5-tetrahydro-imidazol-2-ylideneamino)hexa-1,3,5-triene-1,1-dicarbonitriles (8a—f).—Malononitrile (4 mmol) was added to a solution of compound (5) (2 mmol) in acetonitrile (15 ml), and the reaction mixture stirred at 20 °C for 1 h. The resulting precipitate was filtered off, washed with Et_2O, and dissolved in THF; addition of light petroleum precipitated compound (8). Analytical data for the compounds (8a—f) are given in Table 1.

6-(2,3,4,5-Tetrahydroimidazol-2-ylideneammonio)hexa-1,3,5-triene-1,1-dicarbonitrile Chloride (9).—Compound (1) (2.5 g, 25 mmol) in CH_2Cl_2 (30 ml) was added dropwise during 0.5 h at 20 °C to a solution of pyridine (6 ml) and malononitrile (2.6 g, 0.04 mol) in CH_2Cl_2 (5 ml) under nitrogen. The yellow precipitate was filtered off, washed with CH_2Cl_2 and Et_2O and dried to give (9) (3.7 g, 83%); m.p. 165—168 °C (Found: C, 52.6; H, 4.7; N, 28.4. $C_{11}H_{12}ClN_5$ requires C, 52.9; H, 4.8; N, 28.1%); $v_{max.}$(KBr) 3 320, 3 100, 3 000, 2 800, 2 215, 1 640, 1 570, 1 530, 1 255, 990, and 790 cm⁻¹; m/z 214 (M + 1, 0.2%), 121 (13.4), 120 (20), 92 (29.9), 79 (22.6), 66 (100), and 65 (20.2); δ 3.95 (4 H, CH_2), 6.4 (t 3-H), 6.8 (dd, 5-H), 7.5 (dd, 4-H), 7.85 (d, 2-H), and 8.4 (d, 6-H), $J_{2,3}$ 12.5 Hz, $J_{3,4}$ 12.5 Hz, $J_{4,5}$ 12.7 Hz, $J_{5,6}$ 11.3 Hz.

Reaction of Compound (9) with Phenyl Isocyanate.— Compound (1) (1 g, 4 mmol) and phenyl isocyanate (0.95 g, 8 mmol) in pyridine (15 ml) were stirred at 25 °C for 48 h. To the reaction mixture light petroleum was added (10 ml), and the solid filtered off and washed with Et_2O. The product was triturated with water (20 ml) and filtered to yield a crude solid which was dried and dissolved in THF; the solution was then diluted with light petroleum to precipitate (8a) (0.15 g, 14%), identical with a sample already obtained.

References

1 Part 1: F. Sączewski, *Synthesis*, 1984, 170.
2 J. Becher, *Synthesis*, 1980, 589, and references cited therein.
3 G. Maas and B. Feith, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 511.
4 F. Sączewski and H. Foks, *Synthesis*, 1981, 154.
5 P. Main *et al.*, A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data, Univs. of York, England, and Louvain, Belgium, 1980.
6 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determinations, University of Cambridge, 1976.
7 W. D. S. Motherwell and W. Clegg, PLUTO, Program for Plotting Molecular and Crystal Structures, University of Cambridge, 1978.
8 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
9 M. Jaskólski, 'Collected Abstracts of the Fourth Symposium on Organic Crystal Chemistry,' Poznan, September 1982, pp. 70–71, ed. Z. Kałuski, UAM, Poznań, Poland.
10 J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.
11 Indiana University by Quantum Chemistry Program Exchange No. 141.
12 A. Trani and E. Balasio, *J. Heterocycl. Chem.*, 1974, 11, 257.