Amidino Pentadienylium Salts − A New Cyanine Dye Type

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The reactivity of carboxonium salts permits substitution of one or both of the reactive terminal ethoxy groups by amidino moieties. In this way, new cyanine dyes with extended conjugation paths are obtained. These have been studied by UV/vis spectrophotometry. Furthermore, the X-ray structure of **1b** has been determined and compared with that predicted by molecular mechanical calculations.

Introduction

Polydienylium salts belong to the family of cyanine dyes. They are charged polyenes consisting of an odd-numbered polymethine chain bearing terminal nitrogen atoms. Interest in these structures stems predominantly from their suitability as materials with novel electrical, optical, and mesogenic properties[1]. Attractive characteristics of these dyes are their great variety, their chemical stability, and the relative ease with which they can be prepared, purified, and stored.

Owing to our interest in the preparation and the physicochemical properties of new pentadienylium salts[2], we recently obtained a large variety of new products by reaction of carboxonium salts with nitrogen compounds. In all these products, the degree of conjugation of the pentadienylium structure is extended[3] as a result of the introduction of dicoordinated nitrogen atoms as terminal groups (phosphaimino, amidino, or guanidino) instead of amines. Some related compounds, also bearing amidino substituents, have previously been described by Jutz and Müller[4], but in their case the amidino carbon atom formed part of the pentacarbon backbone.

We present here recent results on pentadienylium salts containing at least one amidino terminal group, as well as the X-ray structure and molecular mechanics of a symmetrical compound belonging to this series.

Carboxonium salts, the starting materials for the syntheses, were prepared and stored under argon. Reactions were carried out in anhydrous acetonitrile at room temperature. We previously demonstrated that it is possible to isolate stable hemicarboxonium intermediates during these reactions[5], which open the way to non-symmetrical compounds. The final products (Scheme 1) **1a**,**b**, **2a**,**b**, **3b** were obtained in yields ranging from 70 to 90% by reaction of *N*,*N*-dimethylbenzamidine or *N*,*N*-dimethyl-*N*′-trimethylsilylbenzamidine with carboxonium or hemicarboxonium salt intermediates under similarly mild reaction conditions.

Since the handling of perchlorate-containing products is potentially hazardous, we currently avoid the use of this anion. Thus, analogous compounds of **1b** and **2b** (**1b**′ and **2b**′) were prepared from carboxonium tetrafluoroborate salts. No changes in the structural and spectral data were apparent. The pentadienylium salts have been fully characterized by NMR, mass (DCI or FAB/MNBA) and UV spectroscopy, as well as by elemental analysis (see Experimental Section). The ^{13}C-NMR and UV/vis data are collected in Tables 1 and 2, respectively.

The ^{13}C-NMR spectra summarized in Table 1 are consistent with the usual charge alternation observed for the chain carbon atoms in the cyanine series[6]. This is due to the electron-withdrawing effect of the end group. The carbon atoms adjacent to nitrogen bear a partial positive charge, whereas a negative charge is observed at the nitrogens and the even-numbered carbon atoms. For the non-symmetrical compounds, the differentiation between C-1 and C-5 or C-2 and C-4 depends on the nature of the terminal group. Thus, in the case of product **3b**, C-2 is strongly coupled with the phosphorus ($^3J_{\text{P-C}}$ = 15.7 Hz) and so is easily assigned.

In their UV/vis spectra (Table 2), 1,5-bis(dialkylamino)-pentadienylium salts exhibit an intense and sharp absorption band in the region 420−450 nm due to the $\pi-\pi^*$ transition of the electrons of the pentadienyl chain. For example, **4** (reference salt) shows an absorption maximum at λ = 444 nm, with ε = 105000 mol^{-1}·l·cm^{-1}. The substi-

1434−193X/98/0202−0329 $ 17.50+.50/0

Scheme 1. General synthetic scheme

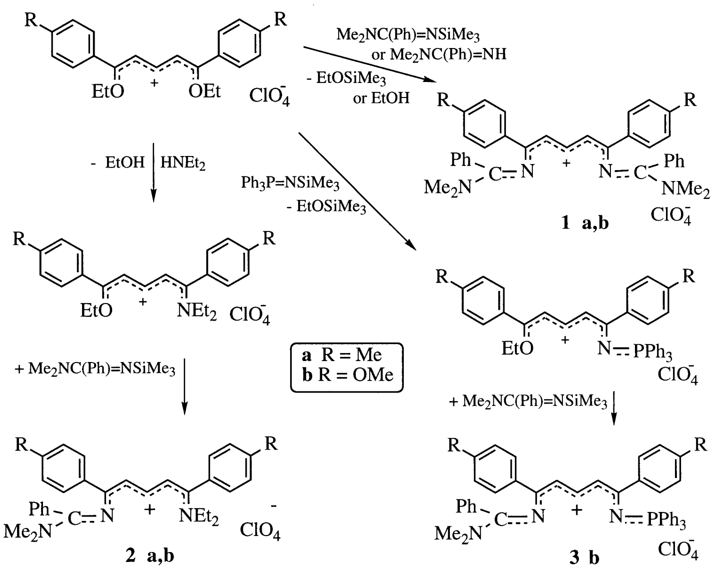


Table 1. ^{13}C-NMR data of the polymethine chain ($CDCl_3$, 50.3 MHz)

	1a	1b	1b′	2a	2b	2b′	3b
C(1)	166.2	165.9	165.8	162.3	162.5	161.3	183.3
C(5)	166.2	165.9	165.8	169.9	169.2	169.4	162.4
C(3)	152.8	152.5	152.5	158.5	158.4	158.4	154.9
C(2)	114.8	114.3	114.1	111.5	106.1	109.3	119.4[a]
C(4)	114.8	114.3	114.1	116.2	111.2	111.2	109.3
C(N)	170.7	170.7	170.8	171.7	172.3	172.0	– [b]

[a] d, J = 15.7 Hz. – [b] Unrecordable.

tution of both diethylamino terminal groups by amidino functions (compounds **1a**, **1b**) increases the length of the conjugation path and extends the charge delocalization. Absorption maxima are consequently shifted to longer wavelengths (570–583 nm), while molar extinction coefficients decrease sharply[7].

Table 2. UV/vis spectra (CH_2Cl_2, 25°C)

	1a	1b	1b′	2a	2b	2b′	3b	4[a]
λ [nm]	570	583	583	522, 495	516, 500	523, 497	537	444
ε [mol·l^{-1}·cm^{-1}]	52000	5500	49700	40500, 30500	43900, 36000	62500, 47900	54000	105000

[a] Reference salt 1,5-methoxyphenyl 1,5-*N*-diethylaminopentadienylium perchlorate (this work).

Compounds **2a**, **2b** (red solutions), which bear only one amidino moiety, exhibit two absorption maxima in an intermediate range (490–530 nm), the sum of the corresponding molar extinction coefficients giving a mean value (about 70000) between those of the corresponding symmetrical salts. Compound **3b** (violet solution) is characterized by twofold substitution, which shifts the maximum to 537 nm and produces a significant decrease in the molar extinction coefficient. The effect of the iminophosphane group is slightly less pronounced, one substitution shifting the maximum to 475 nm, the second to 515 nm. As reported in the literature[7], on extending the conjugation path, the UV spectra of cyanine dyes exhibit a bathochromic shift and a concomitant decrease in absorption.

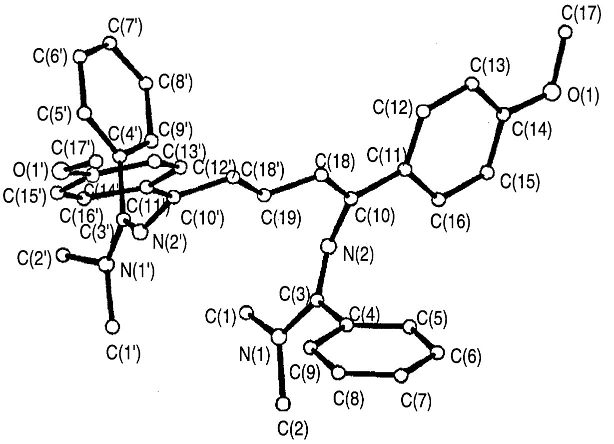
X-ray Solid-State Structure of 1b

The cation in **1b** is distinctly non-planar. As in the case of 1,5-bis(dimethylamino)-1,5-diphenylpentadienylium perchlorate, the central N(2)–C(10)–C(11)–C(18)–C(19)–C(18′)–C(11′)–C(10′)–N(2′) bond system shows only an approximately planar geometry [the deviations from the best least-squares plane are within 0.259(4) Å].

The solid-state structure of compound **1b** confirms the multiple-bond character of the linkages in the chain extending from one dimethylamino nitrogen to the other. The most noteworthy features of the structure are, as expected, associated with the considerable electron density delocalization due to the symmetry of the compound. The distances N(1)–C(3) [1.344(3) Å], C(3)–N(2) [1.303(3) Å], N(2)–C(10) [1.351(3) Å], C(10)–C(18) [1.394(4) Å], and C(18)–C(19) [1.383(3) Å] are significantly shortened in comparison with the standard values of 1.45 for N(sp^2)–C(sp^2) and 1.48 Å for C(sp^2)–C(sp^2) single bonds[8]. Thus, all bonds in the chain show partial double-bond character.

From a stereochemical point of view, this structure exhibits a striking difference in comparison with the other known 1,5-diaryl-substituted cyanine dyes[9]. In most cases, the ni-

Figure 1. A perspective view of cation **1b** with labelling scheme (H atoms are omitted for clarity); the primed atoms are generated from the asymmetric unit using the axis 2



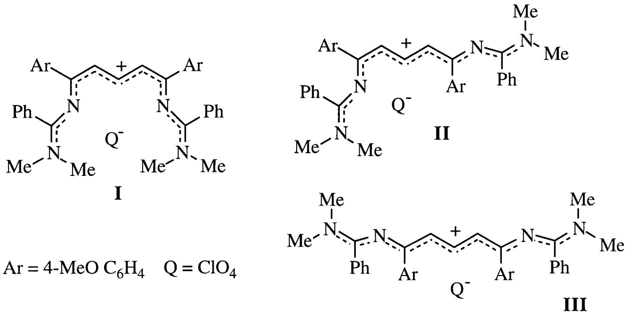
trogen substituents are located in the plane of the chain carbon atoms, whereas the phenyl groups are oriented perpendicular to the chain and are approximately parallel to one another. Compound **1b** shows exactly the reverse situation, with the phenyl groups tending to lie in the only approximate plane through the atoms of the chain, thereby effectively extending it.

The C(11)−C(16) benzene ring is twisted out of this plane by 25.3(2)°, whereas the N(1)−N(2)−C(3)−C(4) moiety is almost orthogonal to the central plane [the corresponding dihedral angle is 71.2(1)°]. In turn, the dihedral angles between the N(1)−N(2)−C(3)−C(4) bond system and the planes of the N(1)−C(1)−C(2) group and of the C(4)−C(9) benzene ring are 55.5(2) and 22.9(4)°, respectively. The bond configuration for atoms N(1), C(3) and C(10) is trigonal planar [the sum of the bond angles is 356.8(8), 359.1(8), and 359.7(6)°, respectively]. A question arose as to whether the delocalized system extends to the amidine moiety or the phenyls in the *trans* configuration. In this regard, two facts seemed contradictory; the strong electronic delocalization in the amidine moiety and the linear position of the phenyl group in relation to the carbon chain. In fact, no extension of conjugation is observed in this direction [C(10)−C(11) length = 1.47 Å] and the π system can be considered as (*Z*)-(*E*)-(*Z*), a situation which has been encountered previously, e.g. in some of our previous work with unsubstituted chains[2a] and in the studies of Reichardt et al. on chiral systems[10].

Cations and anions of **1b** are fixed within the crystal by means of normal van der Waals′ interactions. No shortened intermolecular contacts are observed, the shortest Cl···C, O···C, and C···C distances being 4.048(5), 3.320(4), and 3.442(4) Å, respectively (the corresponding sums of the van der Waals′ radii are 3.50, 3.20, and 3.40 Å[11]).

In an attempt to explain the discrepancy between the structure of **1b** and those of previously studied similar systems, we applied molecular modelling techniques. Calculations were performed with the help of the Discover 95.0 program from Biosym/MSI (San Diego, 1995) on an SG 4D30 or an Indigo 2 Impact 10000 graphics station. For these structures, the choice of accurate potentials for the cyanine chain carbon atoms, and even more so for the nitrogen atoms, is the critical point of all calculations. Two different force fields may be used, i.e. Amber or the general consistent valence force field CVFF. Since they gave comparable results, we will only describe the structural determinations obtained with the latter. Scheme 2 depicts the three main structures calculated: **I** results from a direct calculation starting from a drawing in the usual geometry, **II** can be obtained by a configuration inversion of one of the terminal carbons, and **III**, which corresponds to the previously observed structures in these series, by inversion of both of these.

Scheme 2. Basic models for calculations



Ar = 4-MeO C_6H_4 Q = ClO_4

The final refinement of the structures was obtained after minimization to a r.m.s. (root mean square) gradient of < 0.001 kcal mol^{-1} with the conjugate gradient algorithm of the Discover module. The optimized conformations show energy minima of 374.1 for **I**, 373.5 for **II** and 376.1 kcal for **III**, respectively. The preferred conformations **I** (corresponding to that determined in the solid state) and **II** are separated by just 0.6 kcal in favour of the latter, whereas it would seem that a structure of type **III** can be discarded. To verify this tendency and to explore the whole conformational space, simulated annealing was used: Successive molecular dynamics with temperatures ranging from 3000 to 300°C were performed at 10 ps and the corresponding trajectory was recorded. For each temperature, this allowed selection of one or several minima, for which the corresponding conformers were minimized in order to obtain the lowest energy structure. Among the conformations obtained, none has a type **III** form and no other molecules of type **II** were found with E < 373.5 kcal. The two lowest energy structures shown in Figures 2a and b (371.4 and 371.8 kcal) are of type **I** and differ only in the configuration of the amidine moiety, which resides either on the same side of the cyanine plane (a) or is symmetrically arranged (b). Thus, although it seems possible to find lower energy structures than the X-ray one by molecular modelling, they all exhibit a new molecular arrangement with the aryl substituents of C-1 and C-5 situated in the pseudo-plane of the pentamethine chain. Their differences in energy may be explained by the only approximate potentials used by CVFF (or Amber) to describe the highly-conjugated amidino geometry. An alternative explanation should be found in the packing energy of the solid system, since cyanine dyes are known to exhibit polymorphism[12]. The fact that the UV spectrum of **1b** in solution shows no discrepancy with the others in the series supports this hypothesis. Finally, the optimized geometry of **I** was compared to the solid-state X-ray structure by docking and calculating the r.m.s. deviation in the positions of the chain carbon atoms (0.140 for the superposition of 14 atoms) (Figure 3).

Figure 2. Lowest energy structures of type **I**

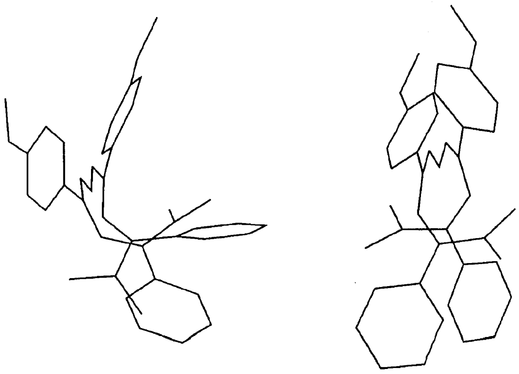
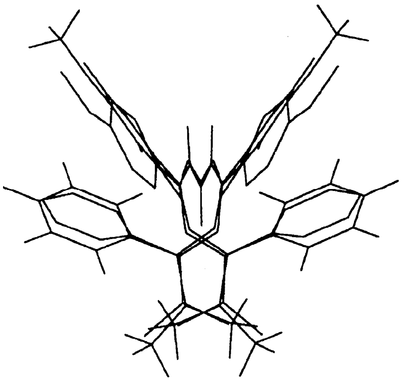


Figure 3. Docking of the optimized conformer **I** and the solid-state structure (H atoms omitted from the latter for clarity)



In conclusion, the novel type of dyes described here introduce a new molecular arrangement with an enhanced conjugated π-system. Symmetrical and non-symmetrical compounds containing this new geometry are currently being tested for their properties in nonlinear optics (NLO).

Experimental Section

Crystal Data Collection: **1b**: $C_{37}H_{39}ClN_4O_6$, $M_r = 671.2$, monoclinic, $a = 18.105(3)$, $b = 16.930(4)$, $c = 12.977(3)$ Å, $\beta = 118.50(1)°$, $V = 34955.7$ Å^3, $Z = 4$, $d_c = 1.28$ g cm^{-3}, space group $C2/c$, $\mu = 1.6$ cm^{-1}, $F(000) = 1416$. All crystallographic measurements were made at ambient temperature (20°C) using an Enraf-Nonius CAD-4 diffractometer operating in the ω.2θ scan mode (the ratio of the scanning rates ω.θ = 1.2). The intensity data were collected within the range $1 \leq \theta \leq 24°$ using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were calculated from the setting angles of 24 strong, high-angle, carefully-centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation control reflections were measured every 200 reflections. Neither significant crystal decay nor movement was noted. Intensities of 2899 (2743 unique) reflections were measured. All data were corrected for Lorentz, polarization, and extinction effects. The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement, 1743 reflections with $I > 4\sigma(I)$ were used. All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with fixed positional and thermal ($B_{iso} = 5$ Å^2) parameters. Convergence was obtained at $R = 0.058$ and $R_w = 0.056$, GoF = 2.09 [unit weighting scheme: 218 refined parameters: largest shift/e.s.d. after final cycle < 0.03; the largest peak in the final difference map, 0.50(4) e/Å^3]. All crystallographic calculations were performed using the SDP-PLUS program package[13] on a PDP-11/23+ computer. Selected distances and valence angles are given in Table 3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected distances and valence angles for **1b**

Atoms	Distances [Å]	Atoms	Angles [°]
N(1)−C(1)	1.462	C(1)−N(1)−C(2)	115.2
N(1)−C(2)	1.467	C(1)−N(1)−C(3)	119.1
N(1)−C(3)	1.344	C(3)−N(2)−C(10)	127.1
N(2)−C(3)	1.303	N(1)−C(3)−N(2)	119.2
N(2)−C(10)	1.351	N(1)−C(3)−C(4)	117.9
C(10)−C(18)	1.394	N(2)−C(3)−C(4)	123.0
C(18)−C(19)	1.383	N(2)−C(10)−C(11)	115.3
C(3)−C(4)	1.487	N(2)−C(10)−C(18)	122.5
C(10)−C(11)	1.470	C(11)−C(10)−C(18)	121.9
		C(10)−C(18)−C(19)	122.7

Experimental Procedure: NMR spectra were obtained with a multinuclear Bruker AC200 spectrometer operating in Fourier transform mode at 200.13 (^{1}H), 81.01 (^{31}P), and 50.32 (^{13}C) MHz. Chemical shifts in $CDCl_3$ are expressed in ppm downfield from internal TMS for ^{1}H and ^{13}C or external 85% H_3PO_4 for ^{31}P, coupling constant are in Hz. − UV/vis spectra were recorded with a Perkin-Elmer lambda-17 spectrophotometer. − All commercial reagents were spectroscopic grade and were used without further purification. As all compounds were synthesized following the same general procedure, only the example of **1a** is described in full.

General Procedure: Preparation of **1a**: A solution of 1.0 g (2.14 mmol) of the carboxonium salt was treated with 0.32 g (2.14 mmol) of commercial N^1,N^1-dimethylbenzamidine or 2.14 mmol of N^1,N^1-dimethyl-N^2-trimethylsilylbenzamidine in 30 ml of anhydrous acetonitrile. The mixture was stirred under argon atmosphere for 5 h at room temperature. After evaporation of the solvent, the residual **1a** was crystallized from ethanol as green prisms.

1,5-Bis(N^1,N^1-dimethylbenzamidino)-1,5-bis(4-methylphenyl)-pentadienylium Perchlorate (**1a**): Yield: 90%, green crystals, m.p. 174°C. − IR: $\tilde{\nu} = 1090$ cm^{-1} (ClO_4). − UV/vis: λ_{max} ⊥ft parenthesislog ε) = 338 nm (15700), 569.5 (52000). − ^{1}H NMR: δ = 2.37 (s, 6 H, MePh), 3.26 (m, 12 H, NMe), 6.16 [d, ^3J(H-H) = 13.2 Hz, 2 H, H-2 and H-4], 7.00−7.40 (m, 19 H, H-3 and Ph). − ^{13}C NMR: δ = 21.5 (s, MePh), 114.8 (s, C-2 and C-4), 128.1−130.6 (m, Ph), 133.8 [s, C (Ph−CN)], 141.6 (s, MePh), 152.8 (s, C-3), 166.2 (s, C-1 and C-5), 170.9 (s, PhCN). − MS (DCI/NH_3); m/z (%): 539 (1)

[M$^+$], 265 (100). – $C_{37}H_{39}ClN_4O_4$ (639.2): calcd. C 69.54, H 6.11; found C 69.12, H 6.18.

1,5-Bis(N^1,N^1-dimethylbenzamidino)-1,5-bis(4-methoxyphenyl)-pentadienylium Perchlorate (**1b**): Yield: 90%, green crystals, m.p. 260°C. – MS (DCI/NH$_3$): *m/z* (%): 571 (1) [M$^+$], 149 (100). – $C_{37}H_{39}ClN_4O_6$ (671.2): calcd. C 66.21, H 5.86, N 8.35; found C 66.08, H 5.83, N 8.33.

1-Diethylamino-5-(N^1,N^1-dimethylbenzamidino)-1,5-bis(4-methylphenyl)pentadienylium Perchlorate (**2a**): Yield: 60%, pink crystals, m.p. 145°C. – MS (DCI/NH$_3$): *m/z* (%): 464 (100) [M$^+$]. – $C_{32}H_{38}ClN_3O_4$ (564.1): calcd. C 68.14, H 6.74, N 7.45; found C 67.62, H 6.91, N 7.12.

1-Diethylamino-5-(N^1,N^1-dimethylbenzamidino)-1,5-bis(4-methoxyphenyl)pentadienylium Perchlorate (**2b**): Yield: 60%, red crystals, m.p. 167°C. – MS (FAB/MNBA): *m/z* (%): 496 (94) [M$^+$]. – $C_{32}H_{38}ClN_3O_6$ (596.1): calcd. C 64.48, H 6.43, N 7.05; found C 63.93, H 6.76, N 6.18.

1-(N^1,N^1-Dimethylbenzamidino)-1,5-bis(4-methoxyphenyl)-5-triphenylphosphazanylpentadienylium Perchlorate (**3b**): Yield: 85%, pink powder, m.p. 147°C. – MS (DCI/NH$_3$) *m/z* (%): 700 (4) [M$^+$], 279 (100) [Ph$_3$PNH$_3$$^+$]; (FAB/MNBA) *m/z* (%): 700 (100) [M$^+$], 262 (27) [Ph$_3$P]. – $C_{46}H_{43}ClN_3O_6P$ (800.3): calcd. C 69.04, H 5.42, N 5.25; found C 68.45, H 5.37, N 5.16.

1,5-Bis(N^1,N^1-Dimethylbenzamidino)-1,5-bis(4-methoxyphenyl)-pentadienylium Tetrafluoroborate (**1b′**): Yield: 85%, green crystals. – MS (FAB/MNBA): *m/z* (%): 571 (100) [M$^+$]. – $C_{37}H_{39}BF_4N_4O_2$ (658.5): calcd. C 67.48, H 5.97, N 8.51; found C 67.57, H 5.90, N 8.32.

1-Diethylamino-5-(N^1,N^1-dimethylbenzamidino)-1,5-bis(4-methoxyphenyl)pentadienylium Tetrafluoroborate (**2b′**): Yield: 80%, red crystals. – MS (DCI/NH$_3$): *m/z* (%): 496 (92) [M$^+$]. – $C_{32}H_{38}BF_4N_3O_2$ (583.5): calcd. C 65.87, H 6.56, N 7.20; found C 65.98, H 6.62, N 7.23.

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