27, 2060 [*J. Org. Chem.*, 1991, No. 10 (Engl. Transl.)].

2. N. P. Papsheva, V. V. Gerasimova, and N. A. Nedolya, *Zh. Org. Khim.*, 1988, **24**, 2230 [*J. Org. Chem.*, 1988, No. 10 (Engl. Transl.)].
3. N. A. Nedolya, V. V. Gerasimova, and N. P. Papsheva, *Zh. Org. Khim.*, 1989, **25**, 2501 [*J. Org. Chem.*, 1989, No. 12 (Engl. Transl.)].
4. N. A. Nedolya, V. V. Gerasimova, N. P. Papsheva, and B. A. Trofimov, *Sulfur Lett.*, 1990, **11**, 227.
5. N. A. Nedolya, N. P. Papsheva, A. V. Afonin, and B. A. Trofimov, *Zh. Org. Khim.*, 1991, **27**, 2239 [*J. Org. Chem.*, 1991, No. 10 (Engl. Transl.)].
6. N. A. Nedolya, N. P. Papsheva, A. V. Afonin, and B. A. Trofimov, *Abstr. of the 5th Seminar-Counsel «Potrebiteli i Proizvoditeli Organicheskikh Reaktivov. Yarmarka Idei»* [*«Users and Manufacturers of Organic Reagents. A Fair of Ideas»*], Dilizhan (Armenia), 1991, 39 (in Russian).
7. N. A. Nedolya, N. P. Papsheva, A. V. Afonin, B. A. Trofimov, V. A. Kukhareva, and T. V. Kashik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2370 [*Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2079 (Engl. Transl.)].
8. B. I. Mikhantyev, V. B. Mikhantyev, V. L. Lapenko, and V. K. Voinova, in: *Nekotorye Vinil'nye Monomery* [*Some Vinylic Monomers*], Izd. Voronezh. Univ., Voronezh, 1970, 60 (in Russian).
9. P. G. Sergeev and S. N. Ivanova, *Zh. Obshch. Khim.*, 1937, **7**, 1495 [*J. Gen. Chem.*, 1937, No. 10 (Engl. Transl.)].
10. N. A. Nedolya, A. V. Afonin, N. P. Papsheva, and B. A. Trofimov, *Zh. Org. Khim.*, 1991, **27**, 2242 [*J. Org. Chem.*, 1991, No. 10 (Engl. Transl.)].
11. N. A. Nedolya, N. P. Papsheva, A. V. Afonin, and B. A. Trofimov, *Abstr. of the 5th Seminar-Counsel «Potrebiteli i Proizvoditeli Organicheskikh Reaktivov. Yarmarka Idei»* [*«Users and Manufacturers of Organic Reagents. A Fair of Ideas»*], Dilizhan (Armenia), 1991, 40 (in Russian).
12. In: *Techniques of Organic Chemistry. Vol. XI. Elucidation of Structures by Physical and Chemical Methods*, Ed. A. Weissberger, Interscience Publishers, New York, 1963, Pt 1, Ch. 6, Table 6.3.
13. T. Mukaiyama, I. Kuwajima, and K. Mizui, *J. Org. Chem.*, 1966, **31**, 32.
14. B. A. Trofimov, M. G. Voronkov, N. A. Nedolya, and V. V. Gerasimova, *Pat. SU 1384576*; *Bull. Izobret.*, 1988, No. 12.
15. A. Albert and E. Serjeant, *Ionization Constants of Acids and Bases*, J. Wiley and Sons, New York, 1962, 179 p.

Received February 27, 1992

Synthesis and structure of novel 2-amino-1,3-dicyano-4-cyclopropyl-6-aryl-1,3-cyclohexadienes

V. N. Nesterov,[a] *G. E. Khoroshilov,*[a] *Yu. T. Struchkov,*[b]* *and Yu. A. Sharanin*[b]

[a]*T. G. Shevchenko Lugansk State Pedagogical Institute,*
348011 Lugansk, Ukraine
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
8 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The reaction of arylmethylenedicyanoacetates with 1,1-dicyano-2-cyclopropylpropene was studied and found to give 2-amino-1,3-dicyano-4-cyclopropyl-6-aryl-1,3-cyclohexadienes. The structure of 2-amino-6-(2-nitrophenyl)-1,3-dicyano-4-cyclopropyl-1,3-cyclohexadiene was corroborated by means of X-ray analysis.

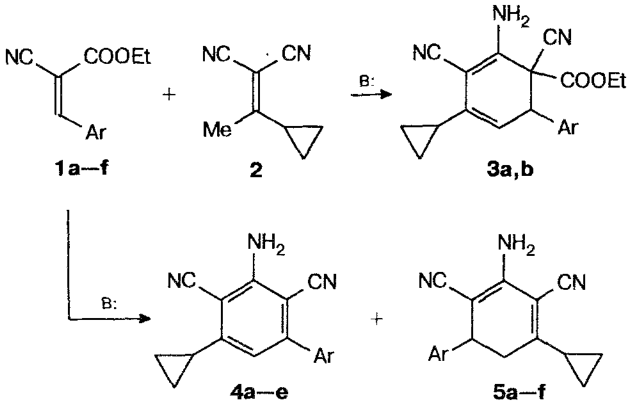
Key words: 1,1-dicyano-2-cyclopropylpropene; cyclohexa-1,3-dienes, polysubstituted; X-ray analysis.

Earlier it was shown that arylmethylenecyanoacetates co-dimerize with substituted 1,1-dicyanopropenes to give 1-amino-2,6-dicyano-6-ethoxycarbonyl-1,3-cyclohexadienes; decarbonylation of the latter leads to the corresponding anilines.[1,2] In order to expand the scope of this reaction we have studied the interaction of aryl(hetaryl)methylenecyanoacetates (**1**) with 1,1-dicyano-2-cyclopropylpropene (**2**) leading to mixtures of anilines[3] (**4**) with 1,3-cyclohexadienes (**5**) as final products. From 4-fluoro- and 4-bromosubstituted arylethylenes **1a,b** we obtained 1-amino-2,6-dicyano-6-ethoxycarbonyl-1,3-cyclohexadienes **3a,b**, easily transformable to **4a,b** and **5a,b**. Reaction of ethyl 2-nitrophenylmethylenecyanoacetate (**1f**) with nitrile **2** gives only 1-amino-2,6-dicyano-5-(2-nitrophenyl)-3-cyclopropyl-1,3-cyclohexadiene (**5f**).

The IR and ^{1}H NMR spectral data corroborate the structure of compounds **3**. Hexadiene **3b** was shown to exist as a mixture with its imino-tautomer (**3b'**) (see the Experimental section). The IR spectral data and the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 355—358, February, 1993.

1066-5285/93/4202-0314$12.50



1, 3, 4, 5: Ar = 4-FC_6H_4 (**a**), 4-BrC_6H_4 (**b**)
1, 4, 5: Ar = Ph (**c**), 4-ClC_6H_4 (**d**), 2-C_4H_3O(furyl) (**e**)
1, 5: Ar = 2-$NO_2C_6H_4$ (**f**)

mixing test with the relevant aromatic amines (prepared by independent procedures) leave no doubt about the structure of 2,6-dicyanoanilines[4] (**4**) (Table 1).

Table 1. Yields, melting points, and the IR spectra of anilines **4a—e**

Compound	Yield (%)	mp (°C)	ν, (cm^{-1})	
			NH_2	CN
4a	20	180—182	3350, 3407	2223
4b	16	215—216	3358, 3402	2224
4c	40	175—177	3360, 3400	2225
4d	41	219—221	3353, 3405	2224
4e	18	218—219	3356, 3398	2220

To confirm the structure of the 1,3-cyclohexadienes **5** thus obtained (Table 2) and to elucidate the possible trends of the reaction, an X-ray structural study of compound **5f** was carried out. The bond angles calculated for the molecule of **5f** are given in Table 3. The general view of this molecule and the relevant bond lengths are presented in Fig. 1.

The substituted cyclohexadiene ring of **5f** is in a half-chair conformation: the C(5) and C(6) atoms are deflected by −0.319(2) Å and 0.375(2) Å from the plane **I** which accomodates the remaining four carbon atoms and includes both of the endocyclic double bonds, within 0.066(1) Å. Moreover, two additional planes can be recognized in the 1,3-cyclohexadiene ring: C(6)C(1)C(2)C(3) (flat within 0.017(1) Å) and C(2)C(3)C(4)C(5) (flat within 0.011(1) Å). They form a dihedral angle (19.1°) arising from a twist about the C(2)—C(3) bond which results from the shortening of intramolecular contacts. We have observed[4] a similar conformation of the cyclohexadiene ring in the sterically congested molecule 1-amino-2,6,6-tricyano-3-cyclopropyl-5-phenyl-1,3-cyclohexadiene (**6**).

Nonbonding interactions force the aryl and the cyclopropyl substituents to deviate by 86.5° and 83.8°, respectively, from plane **I**, whereas the NO_2 group is rotated 138.0° relative to the aromatic ring [a plane exact within 0.002(2) Å passes through the C(13), N(4), O(1), and O(2) atoms].

The molecule of compound **5f** contains a planar fragment [exact within 0.001(1) Å] accomodating five

Table 2. Yields, melting points, IR and ^1H NMR spectral data, and elemental analysis data for cyclohexadienes **5a—f**

Compound	Yield (%)	mp (°C) (solvent used for crystallization)	ν (cm^{-1})		δ						Found / Calculated (%)				Molecular formula
			NH_2	CN	5H, CH cyclopropyl (m)	H(4*a*) (dd)	H(4*e*) (dd)	H(5) (t)	Ar	NH_2 (br.s)	C	H	Hal	N	
5a	21	182—184 (methanol)	3100, 3205, 3208	2160, 2180	0.607, 1.00, 2.03	2.13	2.28	3.68	7.18м	6.26	73.12 73.10	5.09 5.05	6.82 6.80	15.01 15.04	$C_{17}H_{14}FN_3$
5b	18	130—132 (methanol)	3180, 3275, 3320	2170, 2210	0.60, 1.05, 2.05	2.18	2.32	3.68	7.16—7.55m	6.28	59.96 60.02	4.17 4.15	23.51 23.49	12.31 12.35	$C_{17}H_{14}BrN_3$
5c	42	180—181 (methanol)	3150, 3260, 3300	2170, 2190	0.60, 1.09, 2.05	2.19	2.35	3.67	7.27m	6.13	78.08 78.13	5.81 5.79		16.12 16.08	$C_{17}H_{15}N_3$
5d	45	184—185 (methanol)	3210, 3320, 3400	2180, 2200	0.68, 1.10, 2.06	2.18	2.33	3.69	7.21m	6.17	68.98 69.04	4.73 4.77	12.04 11.09	14.25 14.21	$C_{17}H_{14}ClN_3$
5e	41	128—130 (methanol)	3137, 3221, 3270	2176, 2191	0.73, 1.11, 2.12	2.25	2.33	3.74	6.05d, 6.34m, 7.56s	6.24	71.75 71.70	5.26 5.21		16.71 16.72	$C_{15}H_{13}N_3O$
5f	88	190—191 (nitromethane)	3244, 3348, 3420	2185, 2225	0.65, 1.10, 2.10	2.22	2.40	4.13	7.48—8.01m	6.31	66.69 66.66	4.67 4.61		18.19 18.29	$C_{17}H_{14}N_4O_2$

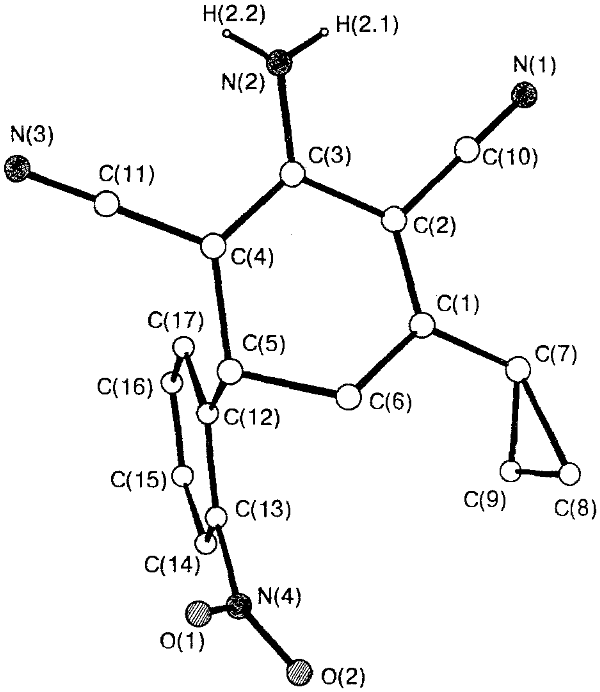


Fig. 1. Molecular structure of compound **5f** (general view) and relevant bond lengths.

atoms and four conjugated bonds, namely, the N(2)—C(3)=C(4)—C(11)≡N(3) moiety. The coordination plane of the trigonal N(2) atom (the sum of whose bond angles is 360°) is nearly coplanar with the above fragment. This favors the p—π conjugation of the unshared electron pair of the N(2) atom with the π-system of the double bond C(3)=C(4). The N(2)—C(3) bond is significantly shorter [1.339(2) Å] in comparison with the unconjugated single N—C(sp^2) bond which is 1.452(4) Å long,[5] but its length is close to that of the conjugated N—C(sp^2) bond (1.336 Å).[6] In compound **6** and in 1-amino-3,5-diphenyl-2,4,4,6,6-pentacyano-1-cyclohexene (**7**) (cf. ref.[7]) the H_2N—C distances in similar conjugated fragments are 1.330(2) Å and 1.348(4) Å, respectively. In **5f** the length of the C(3)=C(4) bond [1.365(2) Å] exceeds the standard length of the C(sp^2)=C(sp^2) bond in the unsubstituted 1,3-cyclohexadiene (1.332 Å).[6] The former bond length is fairly close to 1.355(2) Å for the C(1)=C(2) bond, probably conjugated with the adjacent C(10)≡N(1) cyano group, and close also to the corresponding values of 1.362(3) Å and 1.353(4) Å for molecules **6** and **7**, respectively. The participation of the C(11)≡N(3) cyano group in conjugation is evident from the fact that the length of the C(4)—C(11) bond [1.417(2) Å], is distinctly less than 1.443(2) Å for C(2)—C(10). At the same time, the C(10)≡N(1) and C(11)≡N(3) bonds are of equal length, 1.146(2) Å and 1.148(2) Å (the length of the C≡N bond is usually less sensitive to conjugation). The corresponding lengths of bonds C(sp^2)—C(sp) and C≡N are 1.430(2) Å, 1.149(3) Å and 1.425(4) Å, 1.127(4) Å in **6** and **7**, respectively.

Table 3. Bond angles (φ) in the molecule of compound **5f**

Angle	φ (deg)	Angle	φ (deg)
O(1)—N(4)—O(2)	123.0(2)	C(1)—C(6)—C(5)	112.8(1)
O(1)—N(4)—C(13)	119.7(1)	C(1)—C(7)—C(8)	119.3(1)
O(2)—N(4)—C(13)	117.3(1)	C(1)—C(7)—C(9)	122.1(1)
C(2)—C(1)—C(6)	117.6(1)	C(8)—C(7)—C(9)	58.0(1)
C(2)—C(1)—C(7)	122.6(1)	C(7)—C(8)—C(9)	60.6(1)
C(6)—C(1)—C(7)	119.9(1)	C(7)—C(9)—C(8)	61.4(1)
C(1)—C(2)—C(3)	121.5(1)	N(1)—C(10)—C(2)	176.6(2)
C(1)—C(2)—C(10)	119.5(1)	N(3)—C(11)—C(4)	179.9(2)
C(3)—C(2)—C(10)	118.9(1)	C(5)—C(12)—C(13)	122.8(1)
N(2)—C(3)—C(2)	118.1(1)	C(5)—C(12)—C(17)	122.1(1)
N(2)—C(3)—C(4)	123.9(1)	C(13)—C(12)—C(17)	115.0(1)
C(2)—C(3)—C(4)	118.0(1)	N(4)—C(13)—C(12)	121.2(1)
C(3)—C(4)—C(5)	121.8(1)	N(4)—C(13)—C(14)	115.4(1)
C(3)—C(4)—C(11)	119.3(1)	C(12)—C(13)—C(14)	123.4(1)
C(5)—C(4)—C(11)	118.9(1)	C(13)—C(14)—C(15)	119.1(2)
C(4)—C(5)—C(6)	107.4(1)	C(14)—C(15)—C(16)	119.7(2)
C(4)—C(5)—C(12)	113.7(1)	C(15)—C(16)—C(17)	120.8(2)
C(6)—C(5)—C(12)	111.4(1)	C(12)—C(17)—C(16)	121.8(2)

Steric interaction of the CN group at C(4) with the ajacent *o*-nitrophenyl substituent forces it to rotate around the C(5)—C(12) bond and possibly favors elongation of the C(4)—C(5) bond to 1.518(2) Å as compared to the standard value of 1.504 Å for the C(sp^2)—C(sp^3) bond in 1,3-cyclohexadiene[6] and to the length of the C(1)—C(6) bond [1.496(2) Å]. The aryl substituent is not subjected to any steric effects from the methylene group of the cyclohexadiene ring, so the C(5)—C(6) bond is of ordinary length [1.531(2) Å]. This is much less than 1.568(3) Å for **6** which has two CN groups at the C(6) atom.

In the crystal of **5f** there is a number of intermolecular contacts which are slightly reduced in comparison with the sum of the van der Waals radii of the corresponding atoms: O(1)...C(16) (1−*x*, −*y*, 2−*z*) 3.202(2) Å, O(2)...C(16) (*y*, ½−*y*, −½+*z*) 3.130(2) Å, O(2)...C(17) (*x*, ½−*y*, −½+*z*) 3.159(2) Å (the sum of the van der Waals radii of O and C is 3.22 Å)[8].

Experimental

The IR spectra of compounds **5a—d,f** were recorded in KBr pellets using Perkin-Elmer 577 and Specord 71-IR spectrometers. ^{1}H NMR spectra were recorded on a Bruker WH-100 radiospectrometer (100 MHz) in DMSO-d_6 relative to tetramethylsilane. The purity of the compounds was confirmed by TLC on Silufol UV-254 plates with acetone—hexane (3:5) as the eluent. The mixtures were separated by column chromatography using Silpearl as the adsorbent and acetone—hexane (3:5) as the eluent.

1-Amino-2,6-dicyano-3-cyclopropyl-6-ethoxycarbonyl-5-(4-fluorophenyl)-1,3-cyclohexadiene (3a). To a mixture of **1a** (10 mmol) and **2** (10 mmol) in 15 mL of methanol, one or two drops of morpholine were added with stirring at 20°C. After 90 min of stirring the resulting precipitate was filtered and washed with MeOH and hexane to give 1.9 g (54 %) of **3a**, mp 128—130°C (*i*-PrOH). Found (%): C 68.41; H 5.18; F 5.42;

Table 4. Atom coordinates ($\times 10^4$ for O, N, C, $\times 10^3$ for H) in the structure of **5f**

Atom	*x*	*y*	*z*
O(1)	6640(2)	961(1)	8128(1)
O(2)	4902(2)	2170(2)	7750(1)
N(1)	8549(2)	5868(1)	11806(1)
N(2)	9664(1)	2853(1)	12067(1)
N(3)	9554(1)	−205(1)	11467(1)
N(4)	5582(2)	1565(1)	8312(1)
C(1)	7979(2)	4011(1)	9956(1)
C(2)	8410(2)	3939(1)	10846(1)
C(3)	8950(2)	2810(1)	11253(1)
C(4)	8672(2)	1783(1)	10782(1)
C(5)	7782(2)	1776(1)	9885(1)
C(6)	8165(2)	2925(1)	9381(1)
C(7)	7383(2)	5109(1)	9543(1)
C(8)	5957(2)	5056(1)	8954(1)
C(9)	7395(2)	5325(2)	8533(1)
C(10)	8454(2)	5004(1)	11394(1)
C(11)	9159(2)	685(1)	11161(1)
C(12)	6080(2)	1644(1)	9994(1)
C(13)	5057(2)	1597(1)	9248(1)
C(14)	3519(2)	1585(2)	9335(1)
C(15)	2937(2)	1561(2)	10186(1)
C(16)	3882(2)	1579(2)	10932(1)
C(17)	5431(2)	1636(1)	10839(1)
H(2.1)	972(1)	344(1)	1229(1)
H(2.2)	1006(1)	227(1)	1226(1)
H(5)	821(2)	112(1)	952(1)
H(6.1)	926(2)	289(1)	924(1)
H(6.2)	763(2)	298(1)	879(1)
H(7)	742(2)	576(1)	991(1)
H(8.1)	572(2)	568(1)	904(1)
H(8.2)	550(2)	428(2)	885(1)
H(9.1)	794(2)	473(1)	819(1)
H(9.2)	764(2)	611(1)	839(1)
H(14)	295(2)	158(1)	883(1)
H(15)	192(2)	155(2)	1021(1)
H(16)	361(2)	158(1)	1146(1)
H(17)	605(1)	170(1)	1133(1)

N 11.91. $C_{20}H_{18}FN_3O_2$. Calculated (%): C 68.37; H 5.16; F 5.41; N 11.96. IR spectrum (KBr), ν (cm^{-1}): δ 1620, 3240, and 3402 (NH_2); 2210 and 2270 (C≡N); 1746 (C=O). ^{1}H NMR spectrum (DMSO-d$_6$), δ: 7.10 and 7.50 (both m, 4 H, C_6H_4) overlapping with (2 H, NH_2); 5.07 (d, H, C-4); 4.09 (d, H, C-5, $^3J_{H(4)-H(5)}$ = 3.2 Hz); 1.01 t and 4.12 dd (5 H, C_2H_5O); 1.53 (m, 1 H, CH, cyclopropyl); 0.51 and 0.74 (both m, 4 H, CH_2—CH_2, cyclopropyl).

1-Amino-5-(4-bromophenyl)-2,6-dicyano-3-cyclopropyl-6-ethoxycarbonyl-1,3-cyclohexadiene (3b) and 5-(4-bromophenyl)-2,4-dicyano-3-imino-1-cyclopropyl-4-ethoxycarbonylcyclohexene (3b'). To a stirred mixture of **1b** (10 mmol) and **2** (10 mmol) in 20 mL of MeOH (EtOH) two drops of morpholine were added at 20°C. After 90 min of stirring the precipitate thus formed was filtered and washed with EtOH and hexane to leave 2.75 g (62 %) of **3b**, mp 144—146°C (*i*-PrOH). Found (%): C 58.32; H 4.41; Br 19.41; N 10.16. $C_{20}H_{18}BrN_3O_2$. Calculated (%): C 58.27; H 4.40; Br 19.38; N 10.19. IR spectrum (KBr), ν (cm^{-1}): δ 1630, 3280, 3340, 3420 (NH and NH_2); 2230 and 2275 (C≡N); 1736 (C=O). The ^{1}H NMR spectrum (DMSO-d$_6$) contains the signals of the **amino form** at δ 7.29 and 7.62 (both m, 4 H, C_6H_4) overlapping with the signals of (2 H NH_2); 5.10 (d, H, C-4); 4.11 (d, 1 H, C-5, $^3J_{H(4)-H(5)}$ = 3.3 Hz); 1.07 t and 4.08 dd (5 H, C_2H_5O); 2.18 (m, H, CH, cyclopropyl); 0.50 and 0.80 (both m, 4 H, CH_2—CH_2, cyclopropyl). These signals are accompanied by those of the **imino form** at δ 10.61 and 11.17 (s, H, NH); 7.20—7.70 (m, 4 H, C_6H_4); 3.76 (q, H, C-5); 2.80 (q, H(*e*), C-6); 2.45 (q, H(*a*), C-6); 1.07 t and 4.08 dd (5 H, C_2H_5O); 2.18 (m, H, CH, cyclopropyl); 1.25 (m, 4 H, CH_2—CH_2, cyclopropyl).

3-Aryl-2,6-dicyano-5-cyclopropylanilines (4a—e) and 2-amino-6-aryl-1,3-dicyano-4-cyclopropylcyclohexa-1,3-dienes (5a—f). To 10 mmol of an arylidenecyanoacetate **1a—f** and 10 mmol of dinitrile **2** in 15—20 mL of MeOH or EtOH one or two drops of morpholine were added with stirring at 20°C. When the product of type **3** was precipitated, it was separated by filtration. Then the filtrate (or the native reaction mixture, if no solid was deposited) was left for 4—6 h to afford a mixture of **4a—e** and **5a—e**, which was separated by filtration and washed with EtOH (MeOH) and hexane; in the case of **1f** the same work-up afforded only the diene **5f**. The mixture was separated by column chromatography (see Table 2).

2,6-Dicyano-5-cyclopropyl-3-(4-fluorophenyl)aniline (4a) and 3-amino-2,4-dicyano-1-cyclopropyl-5-(4-fluorophenyl)-1,3-cyclohexadiene (5a). To a stirred solution of **3a** (5 mmol) in 15 mL of MeOH one drop of morpholine was added at 20°C. After 6 h the precipitate that formed was filtered and washed with MeOH and hexane. The mixture was separated by column chromatography to afford 0.5 g of **4a** and 0.61 g of **5a** in 36 % and 44 % yields, respectively. For **4a**: found (%): C 72.34; H 4.41; N 16.82. $C_{15}H_{11}N_3O$. Calculated (%): C 72.28; H 4.45; N 16.86.

The crystals of **3-amino-2,4-dicyano-1-cyclopropyl-5-(2-nitrophenyl)-1,3-cyclohexadiene (5f)** are monoclinic, a = 8.8770(7) Å, b = 11.244(1) Å, c = 14.690(1) Å, β = 91.551(6)°, V = 1465.7(2) Å^3, d_{calc} = 1.388 g cm^{-3}, Z = 4, space group $P2_1/c$. Cell parameters and the intensities of 2587 independent reflections with $I > 2\sigma$ were measured on a four-circle automatic Hilger-Watt diffractometer (20°, λMo K_α, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 60°). The structure was solved by the direct method using the MULTAN program, revealing all non-hydrogen atoms, and refined by the full-matrix regression method in anisotropic approximation for non-hydrogen atoms. All H atoms were localized by differential syntheses and refined isotropically. The final values for variance factors are R = 0.044, R_w = 0.048. All calculations were carried out using an Eclipse S/200 computer and INEXTL programs.[9] Atomic coordinates are given in Table 4 (the data concerning thermal parameters of atoms can be obtained from the authors).

References

1. K. Gewald and W. Schill, *J. Prakt. Chem.*, 1971, **313(4)**, 678.
2. Yu. A. Sharanin, Yu. A. Baskakov, Yu. T. Abramenko, Yu. G. Putsykin, A. F. Vasil'ev, and E. B. Nazarova, *Zh. Org. Khim.*, 1980, **16**, 2192 [*J. Org. Chem.*, 1980, No. 10 (Engl. Transl.)].
3. Yu. A. Sharanin, G. E. Khoroshilov, A. M. Shestopalov, V. N. Nesterov, V. E. Shklover, V. P. Litvinov, Yu. T. Struchkov, and O. M. Nefedov, *Zh. Org. Khim.*, 1991, **27**, 299 [*J. Org. Chem.*, 1991, No. 2 (Engl. Transl.)].
4. V. N. Nesterov, V. E. Shklover, Yu. A. Sharanin, Yu. T. Struchkov, and G. E. Khoroshilov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2776 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2541 (Engl. Transl.)].
5. H. L. Ammon, P. H. Mazzocchi, M. C. Regan, and E. Colicelli, *Acta Crystallogr.*, **B 35**, 1722.

6. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1.

7. V. N. Nesterov, Yu. T. Struchkov, G. E. Khoroshilov, Yu. A. Sharanin, and V. E. Shklover, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2771 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2537 (Engl. Transl.)].

8. A. Bondi, *J. Phys. Chem.*, 1966, **70**, 3006.

9. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, 1983, **28**, 1029 (in Russian).

Received March 30, 1992

Photolysis of 2-dialkylamino-3-amino(or alkylamino)-1,4-naphthoquinones

V. N. Berezhnaya,* V. P. Vetchinov, R. P. Shishkina, and V. I. Mamatyuk

Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences,
9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 4752

Using ^{1}H and ^{13}C NMR spectroscopy, naphthodihydroimidazolediols were identified as the primary products of photolysis of 2-dialkylamino-3-amino(alkylamino)-1,4-naphthoquinones. Their further non-photochemical («thermal») transformations depend on their structure and on the photolysis conditions.

Key words: 2-dialkylamino-3-amino(alkylamino)-1,4-naphthoquinones, photolysis; primary products, identification.

Naphthoimidazolediones and their dihydro derivatives have been isolated earlier during preparative-scale photolyses of 2-dialkylamino-1,4-naphthoquinones.[1,2] In the case of 2-(4-benzoylpiperazino)-3-aminonaphthoquinone, an enaminonaphthoquinone was obtained,[2] along with a naphthoimidazoledione, while the irradiation of the respective 2-dimethylamino naphthoquinone afforded the product of its dealkylation.[1] Since the formation of enaminoquinones and their dealkylation products was observed upon the decomposition of naphthodihydrooxazoles,[3,4] it has been suggested that the primary products formed in the photolysis of 2-dialkylamino-3-amino-1,4-naphthoquinones could be naphthodihydrooxazoles, as in the case of their 3-unsubstituted analogs.[2] The purpose of the present work was to detect the formation of the postulated intermediates using NMR spectroscopy; this approach has been already described by us in a detailed account.[4]

The low-temperature photolysis of 2-piperidino-3-amino-1,4-naphthoquinone (**1a**) carried out both in CS_2 and in DMSO-d_6 under argon (−90°C, $\lambda > 400$ nm), yields a product which has been identified (at ~20°C) as 1,2,3,4,4a,5-hexahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyridine-6,11-diol (**2a**) (Scheme 1). Our attempts to record the low-temperature spectrum of the photolysis product obtained from compound **1a** were unsuccessful. However, such a spectrum has been recorded for the photolysis product derived from 2-(1-piperidino)-3-ethylamino-1,4-naphthoquinone (**1b**). It has been found that the low-temperature photolysis of naphthoquinone **1b** in polar media (in the DMSO-d_6 matrix at −53°C or in a toluene-d_8 — methanol-d_4 (1:1) mixture at −78°C), under argon leads to 5-ethyl-1*H*-2,3,4,4a-tetrahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyridine-6,11-diol (**2b**) (Scheme 1). Using the toluene-d_8 — methanol-d_4 solvent mixture, we managed to obtain the low-temperature ^{1}H and ^{13}C NMR spectra of compound **2b**. The NMR spectra of the same sample, recorded at 20°C, prove that **2b** is stable under an inert atmosphere. In the ^{1}H NMR spectrum of the dihydroimidazolediol **2b** the CH_2 protons of the N-ethyl group have different chemical shifts (CS), at 3.40 ppm and 4.02 ppm. This points to the formation of a dihydroimidazole ring. The CH group common to both of the newly formed rings is revealed in the ^{1}H NMR spectrum by the one-proton signal, H(4a)*, which appears as a doublet of doublets ($J_{\mathrm{H(4a)-H(4}a)}$ = 10.3 Hz, $J_{\mathrm{H(4a)-H(4}e)}$ = 2.6 Hz) at 4.26 ppm. This confirms the structure of the dihydroimidazole ring and indicates that the H(4a) atom occupies a quasi-axial position in the piperidine ring. The absence of signals in

---

* The following symbols are used: *a* — axial, *e* — equatorial, a — according to nomenclature.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 358—362, February, 1993.