CYCLIZATION OF NITRILES.

41.* REACTION OF ARYLMETHYLENEMALONONITRILES WITH MALONONITRILE; CRYSTAL STRUCTURE OF 1-AMINO-3,5-DIPHENYL-2,4,4,6,6-PENTACYANO-1-CYCLOHEXENE

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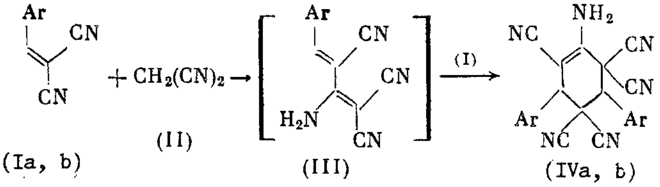
UDC 66.095.252:547.461.
3:547.737:547.592.2

1-Amino-3,5-diaryl-2,4,4,6,6-pentacyano-1-cyclohexenes are prepared by reaction of arylmethylenemalononitriles with malononitrile. The cyclohexene ring of (IVa) has a distorted $N^2{-}C^1{=}C^2{-}C^7{\equiv}N^1$ fragment. Steric effects in (IVa) cause a substantial increase in $C^6{-}C^1$ and $C^3{-}C^4$ bond length to 1.546(4) and 1.570(4) Å, respectively.

Depending on the synthesis conditions, the structure, and ratio of reagents, reaction of arylmethylenemalononitriles with malononitrile can give different reaction products. Michael adducts [2], more highly transformed products such as 2-alkoxy-, 2-amino-, and 2-halo-6-aminopyridines [3], and anilines [4] are possible. However, we first showed that reaction of nitriles (Ia and Ib) and (II) at a 2:1 ratio in 2-propanol under the action of morpholine unexpectedly forms 1-amino-3,5-diaryl-2,4,4,6,6-pentacyano-1-cyclohexenes (IVa and IVb)



(I), (IV): Ar = C_6H_5 (a); $3\text{-}FC_6H_4$ (b).

The reaction can be described as addition of malononitrile (II) to one of the nitrile groups of the arylmethylenemalononitrile (Ia and Ib) with generation of the intermediate butadiene (III). The molecule of (III) further reacts as a diene through a [4 + 2]-cycloaddition reaction with unbound nitrile (Ia and Ib) acting as a dienophile to give cyclohexene (IVa and IVb).

We carried out an x-ray study of (IVa) as a 1:1 solvate with ethylacetate. The molecule is actually 1-amino-3,5-diphenyl-2,4,4,6,6-pentacyano-1-cyclohexene (Fig. 1).

DISCUSSION

The cyclohexene ring in (IVa) has a distorted half-chair conformation. Atoms C^4 and C^5 deviate from the plane of the remaining four ring atoms (with an accuracy not less than 0.004(3) Å) by 0.543(3) and −0.223(3) Å, respectively.

Conjugation in the plane [deviations of the atoms from the average plane do not exceed 0.007(3) Å] of the fragment N^2, C^1, C^2, C^7, N^1 includes the $C^1{=}C^2$ double bond and the NH_2 and CN groups bound to it. In fact, the coordination plane of the trigonal planar atom N^2 (sum of angles is 360°) is approximately coplanar with this fragment. This is favorable for p–π-conjugation of the unshared electron pair of atom N^2 with the π-system of the $C^1{=}C^2$ double bond. The $N^2{-}C^1$ bond length of 1.348(4) Å is short in comparison with the stand-

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*For previous communication, see [1].

A. N. Nesmeyanov Institute of Organoelemental Compounds, Academy of Sciences of the USSR, Moscow. T. G. Shevchenko Voroshilovgrad State Pedagogical Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2771-2775, December, 1989. Original article submitted October 4, 1988.

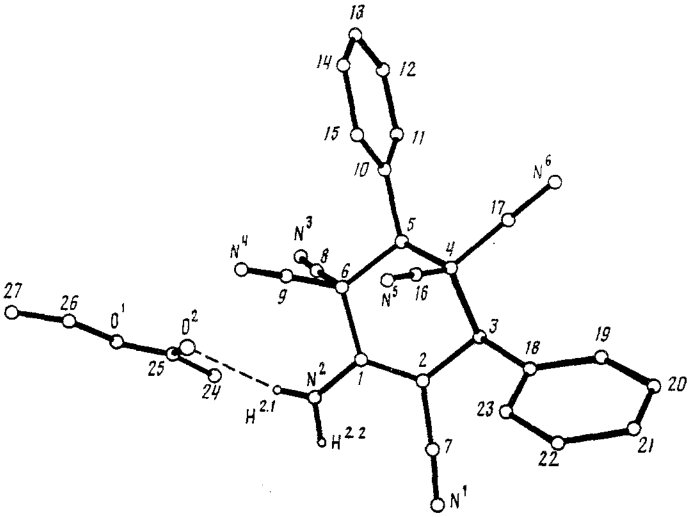

Fig. 1. Asymmetric unit of the solvate (IVa)·MeCOOEt.

TABLE 1. Short Nonbonded Contacts in (IVa)*

Distance	d, Å	Distance	d, Å
$N^2...C^7$	2.760(4)	$C^9...C^{16}$	3.005(5)
$N^2...C^8$	2.834(4)	$C^{10}...C^{16}$	3.200(5)
$N^2...C^9$	2.902(4)	$C^{10}...C^{17}$	2,893(5)
$C^7...C^{18}$	2,909(4)	$C^{15}...C^{16}$	3,181(5)
$C^7...C^{23}$	3.032(4)	$C^{15}...C^{17}$	3,388(5)
$C^8...C^{10}$	2,993(4)	$C^{16}...C^{18}$	2,939(5)
$C^8...C^{11}$	3,359(5)	$C^{16}...C^{23}$	3.106(5)
$C^9...C^{10}$	3,014(4)	$C^{17}...C^{18}$	3,004(5)
$C^9...C^{15}$	3,142(5)	$C^{17}...C^{19}$	3,228(5)

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*The sum of van der Waals radii of N and C is 3.21 Å. The doubled van der Waals radius of C is 3.42 Å [8, 9].

ard length of an ordinary $N-C_{sp^2}$ bond of 1.452(4) Å [5]. It is comparable to the 1.336 Å [6] length of a conjugated $N-C_{sp^2}$ bond with inclusion of a trigonal planar nitrogen atom. The $C^1=C^2$ bond length in turn is increased to 1.353(4) Å in comparison with the standard $C_{sp^2}=C_{sp^2}$ bond length of 1.326 Å [6] in unsubstituted cyclohexene. Inclusion of the CN group in the conjugation, as supported by IR data, leads to a $C_{sp^2}-C_{sp}$ bond length of 1.425(4) and a C≡N length of 1.134(4) Å. These lengths are similar to those found in TCNQ (1.427 and 1.144 Å) [6] and in the nitrile of 3-amino-2,4-di(pyridyn-2-yl)crotonic acid, the dimerization product of 2-pyridylacetonitrile [1.425(4) and 1.156(3) Å] [7]. According to the authors, the nitrile group participates in the conjugation.

The short nonbonded contact $N^2...C^7$ of 2.760(4) Å (Table 1, the sum of van der Waals radii of N and C is 3.21 Å [8, 9]) causes the $C^2C^1N^2$ bond angle to increase to 125.5(3)°. The $C^1C^2C^7$ angle [115.8(3)°] does not increase in comparison to the $C^3C^2C^7$ angle [117.6(3)°] since the CN group on C^2 interacts sterically with the pseudoaxial phenyl substituent $C^{18}...C^{23}$. The ring of this substituent and the benzene ring of the other phenyl substituent $C^{10}...C^{15}$ are rotated relative to the plane of the cyclohexene ring by 88.5 and 119.9°. This rotation controls the nonbonded interaction of these rings with other substituents in the cyclohexene ring (Table 1 and Fig. 2).

The data of Table 1 clearly show that the steric effect of (IVa) explains both the substantial increase in C^6-C^1 and C^3-C^4 bond length to 1.546(4) and 1.570(4) Å and the less obvious increase in C^2-C^3, C^4-C^5, and C^5-C^6 bond lengths to 1.523(4), 1.546(4), and 1.547(4) Å, respectively, in comparison to the standard values of the $C_{sp^2}-C_{sp^3}$ and $C_{sp^3}-C_{sp^3}$ bond lengths in unsubstituted cyclohexene of 1.506 and 1.541 Å [6]. Moreover, the electron-accepting CN group probably affects these bond lengths, for example, as indicated by the long C^6-C^1 bond of the C^6 atom that has two CN groups in comparison to the C^2-C^3 bond at the C^2 atom that has one CN group conjugated to the double bond.

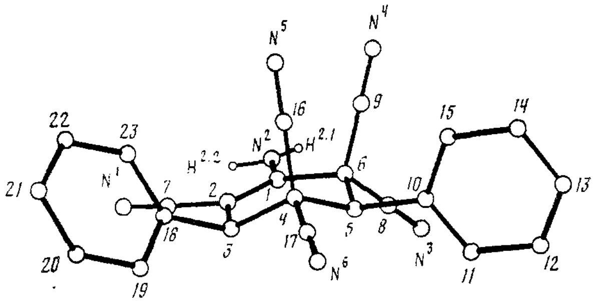

Fig. 2. Mutual orientation of substitutions in (IVa).

TABLE 2. Atomic Coordinates ($\cdot 10^4$ for O, N, C; $\cdot 10^3$ for H)

Atom	X	Y	Z
O^1 *	9994(2)	4921(13)	3626(2)
O^2 *	8157(2)	4502(5)	2862(2)
N^1	5394(2)	457(5)	−373(1)
N^2	6619(2)	2224(5)	1542(1)
N^3	7115(2)	250(6)	3592(2)
N^4	5103(3)	5425(5)	2811(2)
N^5	2417(3)	4194(5)	1612(2)
N^6	1288(3)	−1540(6)	2226(2)
C^1	5548(2)	1443(5)	1636(2)
C^2	4743(2)	550(5)	1035(2)
C^3	3547(2)	−405(5)	1130(2)
C^4	3133(2)	503(5)	1911(2)
C^5	4181(2)	367(5)	2662(2)
C^6	5288(3)	1603(5)	2523(2)
C^7	5080(3)	458(5)	243(2)
C^8	6340(3)	852(5)	3123(2)
C^9	5176(3)	3754(5)	2695(2)
C^{10}	3837(3)	663(5)	3502(2)
C^{11}	4148(3)	−809(6)	4091(2)
C^{12}	3891(3)	−613(7)	4873(2)
C^{13}	3303(3)	1069(7)	5070(2)
C^{14}	2942(3)	2525(7)	4495(2)
C^{15}	3228(3)	2314(6)	3710(2)
C^{16}	2728(3)	2587(6)	1749(2)
C^{17}	2087(3)	−658(6)	2092(2)
C^{18}	2562(2)	−219(5)	365(2)
C^{19}	1761(3)	−1802(6)	160(2)
C^{20}	813(3)	−1618(7)	−510(2)
C^{21}	668(3)	91(7)	−976(2)
C^{22}	1464(3)	1631(7)	−784(2)
C^{23}	2409(3)	1496(6)	−111(2)
C^{24} *	9655(4)	1987(8)	2877(3)
C^{25} *	9167(3)	3918(6)	3105(2)
C^{26} *	9633(4)	6855(8)	3869(3)
C^{27} *	10708(5)	7756(10)	4418(3)
$H^{2.1}$	717(2)	278(5)	187(2)
$H^{2.2}$	685(2)	209(5)	102(2)
H^3	371(2)	−189(5)	128(1)
H^5	446(2)	−71(4)	267(1)
H^{11}	468(2)	−161(4)	403(1)
H^{12}	427(3)	−188(8)	524(2)
H^{13}	308(2)	126(5)	561(2)
H^{14}	237(3)	384(6)	460(2)
H^{15}	297(2)	323(5)	335(2)
H^{19}	201(2)	−319(5)	48(2)
H^{20}	33(2)	−275(5)	−63(2)
H^{21}	−3(3)	26(7)	−146(2)
H^{22}	134(2)	291(5)	−116(2)
H^{23}	309(3)	254(6)	−2(2)
$H^{24.1}$ *	880(3)	106(8)	238(2)
$H^{24.2}$ *	999(3)	91(7)	333(2)
$H^{24.3}$ *	1035(4)	223(10)	267(3)
$H^{26.1}$ *	886(3)	655(6)	424(2)
$H^{26.2}$ *	921(3)	758(6)	342(2)
$H^{27.1}$ *	1045(4)	963(10)	467(3)
$H^{27.2}$ *	1148(4)	779(9)	398(2)
$H^{27.3}$ *	1097(3)	688(7)	490(2)

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*Atoms of the ethylacetate solvate molecule.

The C_{sp^3}–C_{sp} and C≡N bond lengths in the cyano groups at the C^4 and C^6 atoms lie in the ranges 1.481-1.486(5) and 1.127-1.145(5) Å, respectively. These are similar to the standard values of 1.470 and 1.136 Å [6].

A hydrogen bond N^2–$H^{2.1}$...O^2 (x, y, z) forms with the ethylacetate solvate molecule in the crystal of (IVa) [N^2...O^2, 2.945(4); N^2–$H^{2.1}$, 0.83(3); $H^{2.1}$...O^2, 2.14(3) Å; N^2–$H^{2.1}$...O^2, 164(3)°] (Fig. 1). The second hydrogen atom $H^{2.2}$ of the amino group does not form hydrogen bonds or short intermolecular contacts.

EXPERIMENTAL

IR spectra were taken as KBr pellets on a UR-20 spectrometer. PMR spectra were recorded on a Bruker WH-100 instrument (100 MHz) in DMSO-d_6 with an internal standard of TMS. TLC was carried out using methylethylketone:hexane (3:5) on Silufol UV-254 plates.

Crystals of the solvate (IVa)·MeCOOEt are monoclinic, at 20°C a = 11.2347(13), b = 6.7203(6), c = 16.4704(10) Å, β = 100.575(8)°, V = 1222.4(6) $Å^3$, d_{calc} = 1.257 g/cm^3, Z = 2, space group $P2_1$. Cell constants and intensities of 2292 independent reflections were measured on a Hilger Watts 4-cycle automatic diffractometer (λ MoKα, graphite monochromator, θ/2θ scanning up to θ_{max} = 30°). The structure was solved by direct methods using MULTAN and was refined by anisotropic full matrix least squares for nonhydrogen atoms for 2110 reflections with I ≥ 2σ. Hydrogen atoms were located in a difference synthesis and refined isotropically. The final values of the agreement factors were R = 0.043 and R_w = 0.036. All calculations were carried out on an Eclipse S/200 computer using INEXTL programs [10]. The atomic coordinates are given in Table 2 [isotropic equivalent thermal parameters for nonhydrogen atoms (isotropic for H atoms) can be obtained from the authors].

1-Amino-3,5-diphenyl-2,4,4,6,6-pentacyano-1-cyclohexene (IVa). Benzylidenemalononitrile (Ia, 1.56 g, 10 mmoles) and malononitrile (II, 0.33 g, 5 mmoles) were dissolved in 30 ml 2-propanol and morpholine (5 drops) was added. The mixture was stirred for 2 h at 20°C. The precipitate was filtered off and washed with 2-propanol and hexane. Yield 1.4 g (75%) of (IVa), mp 231-233°C (from 2-propanol). IR spectrum (KBr, ν, cm^{-1}): 2207 (CN_{conj}, strong), 2256 ($CN_{nonconj}$, weak), 2915 and 2948 (CH), 3374 and 3468 (NH_2), 1636 (δNH_2). PMR spectrum (DMSO-d_6, δ, ppm): 4.87 s (1H, C^5H), 5.16 s (1H, C^3H), 7.4-7.9 m (12H, NH_2, and 2-C_6H_5). Found: C, 73.78; H, 3.77; N, 22.45%. $C_{23}H_{14}N_6$. Calculated: C, 73.82; H, 3.53; N, 22.49%.

1-Amino-3,5-di(3-fluorophenyl)-2,4,4,6,6-pentacyano-1-cyclohexene (IVb). This was prepared analogously from 3-fluorobenzylidenemalononitrile (Ib, 1.74 g, 10 mmoles) and malononitrile (II, 0.33 g, 5 mmoles). Yield 1.6 g (78%) of cyclohexene (IVb), mp 219-221° (from 2-propanol). IR spectrum (KBr, ν, cm^{-1}): 2204 (CN_{conj}, strong), 2253 ($CN_{nonconj}$, weak), 2923 and 2953 (CH), 3378 and 3473 (NH_2), 1635 (δNH_2). PMR spectrum (DMSO-d_6, δ, ppm): 4.87 s (1H, C^5H), 5.32 s (1H, C^3H), 7.2-7.8 m (8H, 2-C_6H_4), 8.17 br. s (2H, NH_2). Found: C, 66.84; H, 2.80: F, 9.63; N, 20.36%. $C_{23}H_{12}F_2N_6$. Calculated: C, 67.02; H, 2.91; F, 9.72; N, 20.32%.

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