X-RAY DIFFRACTION STUDY OF 6-METHYL-4,6-DIPHENYL-2-DICYANOMETHYLENE-1,2,5,6-TETRAHYDRONICOTINONITRILE

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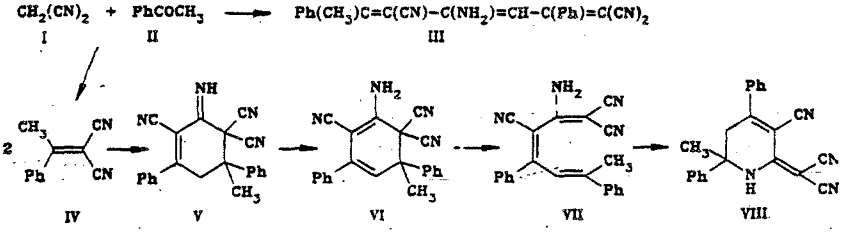
It was demonstrated by x-ray diffraction analysis that 1-imino-5-methyl-3,5-diphenyl-2-cyclohexene-2,6,6-tricarbonitrile, which has been erroneously described in the literature as a 1-phenylethylidenemalononitrile dimer, actually has the 6-methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile structure. The latter is one of three isomers that are formed as a result of the base-catalyzed dimerization of 1-phenylethylidenemalononitrile. The conformation of the unsaturated heteroring is discussed.

In an investigation of the base-catalyzed reaction of malononitrile (I) with acetophenone (II) Anderson and co-workers [1] obtained a compound, to which the 4-amino-2,6-diphenylhepta-1,3,5-triene-1,1,5-tricarbonitrile (III) structure was assigned, although this formula is not in agreement with the IR spectrometric data [1, 2].



$$\underset{I}{CH_2(CN)_2} + \underset{II}{PhCOCH_3} \longrightarrow \underset{III}{Ph(CH_3)C{=}C(CN){-}C(NH_2){=}CH{-}C(Ph){=}C(CN)_2}$$

IV V VI VII VIII

The same compound was obtained as a result of the base-catalyzed dimerization of 1-phenylethylidenemalononitrile (IV) in alcohol solution, for which alternative structure V was proposed on the basis of the PMR spectra, and the identical character of III and V was established [2].

Abramenko and co-workers later [3] accomplished the dimerization of nitrile IV in ether and obtained the 1-amino-5-methyl-3,5-diphenylcyclohexa-1,3-diene-2,6,6-tricarbonitrile dimer (VI) sought in [2], which was then subjected to base-catalyzed recyclization to 6-methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile (VIII), which was identical to the III and V described in [1, 2]; intermediate 2-amino-4,6-diphenylhepta-1,3,5-triene-1,1,3-tricarbonitrile (VII) was also obtained [3].

Although the formulas of isomers VI-VIII are in agreement with the IR, Raman, and NMR spectra presented in [3], it was necessary to unambiguously establish the presence of nitrogen in the ring of VIII. This is due not so much to the contradictory data on the structure of the 1-phenylethylidenemalononitrile dimer, to which alternative structures V and VIII were assigned [2, 3], as to the necessity to unambiguously prove the general character [4, 5] of the new reaction – the recyclization of dimer VI through the intermediate formation of triene VII to nicotinonitrile VIII. In addition to its theoretical significance, this reaction is also finding practical application in view of the recent use of a derivative of triene VII for the synthesis of o-amino nitriles that fluoresce strongly [6].

In the present paper we present the results of x-ray diffraction analysis of the same substance obtained by three different methods [1-3], which is represented in the literature by the alternative formulas III [1], V [2], and VIII [3]. The identical character of V and VII was established in [3].

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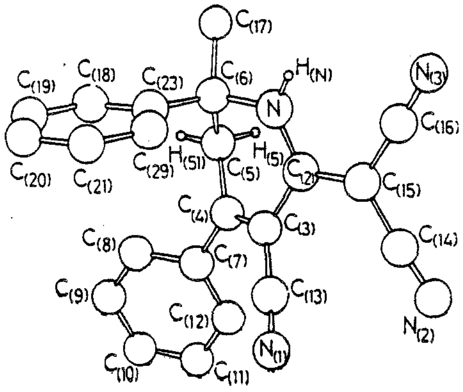
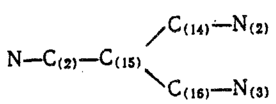


Fig. 1. Three-dimensional model of the 6-methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile (VIII) molecule.

The results of x-ray diffraction analysis of a single crystal of V obtained by the method in [2] showed that the final product of the base-catalyzed transformation of 1-phenylethylidenemalononitrile (IV) in alcohol has the 6-methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile structure (VIII) [3] rather than the iminocyclohexene structure V, as previously assumed in [2].

A three-dimensional model of the VIII molecule and the numbering of the atoms, the coordinates of which are given in Table 1, are shown in Fig. 1. The numbers of the $C_{(24)} \ldots C_{(29)}$ atoms correspond to the atoms of the benzene molecule that is cocrystallized with the VIII molecule in a ratio of 1:1. The valence bonds are presented in Table 2, and the valence angles are presented in Table 3.

The length of the $N-C_{(2)}$ bond [1.333(8) Å] is much shorter than the length of a nitrogen–carbon single bond, while the $C_{(2)}-C_{(15)}$ bond is appreciably longer than the ordinary carbon–carbon double bond in similar systems. These data, together with the decrease in the $C_{(14)}-C_{(15)}$ distance as compared with the $C_{(3)}-C_{(13)}$ distance, constitute evidence that the distribution of the π-electron density in the fragment under consideration



is adequately described not by formula VIII but rather by the superimposition of resonance structures a-c.

TABLE 1. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$) and Hydrogen Atoms ($\cdot 10^3$) in the 6-Methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile Structure

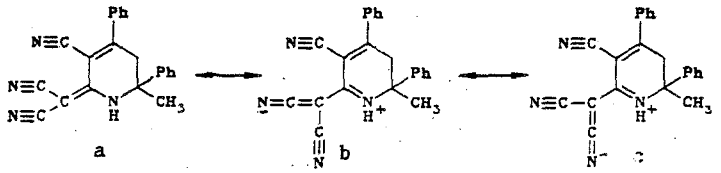
Atom	x	y	z	Atom	x	y	z
N	6790(5)	2467(4)	4184(4)	$C_{(22)}$	9465(7)	1659(7)	2237(6)
$N_{(1)}$	4398(6)	−1523(6)	−1970(5)	$C_{(23)}$	8216(6)	2010(5)	2680(5)
$N_{(2)}$	2575(6)	0217(6)	4023(5)	$C_{(24)}$	333(1)	351(1)	0132(8)
$N_{(3)}$	3767(6)	4395(5)	5271(5)	$C_{(25)}$	303(1)	245(1)	0516(9)
$C_{(2)}$	5831(6)	1518(5)	3937(4)	$C_{(26)}$	2993(9)	286(1)	1714(8)
$C_{(3)}$	6304(6)	0084(5)	3346(5)	$C_{(27)}$	324(1)	420(1)	2360(8)
$C_{(4)}$	7702(6)	−0297(6)	3432(5)	$C_{(28)}$	358(1)	515(1)	1988(9)
$C_{(5)}$	8741(6)	0806(6)	4083(5)	$C_{(29)}$	3591(9)	484(1)	0885(8)
$C_{(6)}$	8243(6)	2158(6)	3894(5)	$H_{(N)}$	659(4)	323(4)	444(3)
$C_{(7)}$	8268(7)	−1739(6)	2946(5)	$H_{(5)}$	878(4)	094(4)	489(3)
$C_{(8)}$	9473(7)	−1996(7)	2442(7)	$H_{(8)}$	992(7)	−130(6)	230(5)
$C_{(9)}$	10005(9)	−3337(8)	1947(8)	$H_{(9)}$	109(1)	−364(9)	151(7)
$C_{(10)}$	9347(9)	−4413(8)	1997(8)	$H_{(10)}$	978(8)	−538(8)	161(6)
$C_{(11)}$	8182(9)	−4175(6)	2516(7)	$H_{(11)}$	773(5)	−488(5)	260(4)
$C_{(12)}$	7608(7)	−2835(6)	2995(6)	$H_{(12)}$	671(5)	−272(5)	335(4)
$C_{(13)}$	5242(7)	−0841(6)	2600(5)	$H_{(17)}$	878(5)	420(5)	458(4)
$C_{(14)}$	3471(6)	0910(6)	4107(5)	$H_{(18)}$	620(5)	245(5)	231(4)
$C_{(15)}$	4496(6)	1875(6)	4239(5)	$H_{(19)}$	620(6)	208(5)	037(4)
$C_{(16)}$	4084(7)	3267(6)	4807(5)	$H_{(20)}$	82(1)	160(9)	−044(7)
$C_{(17)}$	9148(7)	3329(6)	4704(6)	$H_{(21)}$	1036(6)	128(6)	089(5)
$C_{(18)}$	7008(7)	2197(6)	1978(5)	$H_{(22)}$	1025(5)	156(5)	272(4)
$C_{(19)}$	7031(8)	2052(7)	0895(6)	$H_{(51)}$	975(5)	055(4)	390(4)
$C_{(20)}$	8265(8)	1695(8)	0443(6)	$H_{(171)}$	1012(5)	312(4)	463(4)
$C_{(21)}$	9487(7)	1517(8)	1147(6)	$H_{(172)}$	918(7)	345(7)	564(5)

TABLE 2. Principal Valence Distances in the 6-Methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile Structure

Bond	Length, Å	Bond	Length, Å	Bond	Length, Å
$N—C_{(6)}$	1,477(7)	$C_{(5)}—H_{(51)}$	1,02(5)	$C_{(7)}—C_{(8)}$	1,384(9)
$N—C_{(2)}$	1,333(7)	$C_{(5)}—C_{(4)}$	1,500(7)	$C_{(3)}—C_{(2)}$	1,472(7)
$N—H_{(N)}$	0,75(2)	$C_{(4)}—C_{(3)}$	1,347(6)	$C_{(3)}—C_{(13)}$	1,438(7)
$C_{(6)}—C_{(17)}$	1,518(7)	$C_{(4)}—C_{(7)}$	1,483(7)	$C_{(13)}—N_{(1)}$	1,132(7)
$C_{(6)}—C_{(23)}$	1,524(8)	$C_{(7)}—C_{(12)}$	1,390(8)	$C_{(2)}—C_{(15)}$	1,377(8)
$C_{(6)}—C_{(5)}$	1,524(7)	$C_{(12)}—C_{(11)}$	1,398(9)	$C_{(15)}—C_{(14)}$	1,424(7)
$C_{(16)}—N_{(3)}$	1,143(7)	$C_{(11)}—C_{(10)}$	1,363(9)	$C_{(14)}—N_{(2)}$	1,145(7)
$C_{(5)}—H_{(5)}$	1,00(4)	$C_{(9)}—C_{(8)}$	1,389(10)	$C_{(15)}—C_{(16)}$	1,419(7)

TABLE 3. Some Valence Angles in the 6-Methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile Structure

Atoms	Angle, deg	Atoms	Angle, deg	Atoms	Angle, deg
$C_{(2)}—N—C_{(6)}$	124,3(4)	$C_{(3)}—C_{(4)}—C_{(5)}$	117,7(5)	$N—C_{(6)}—C_{(23)}$	110,5(5)
$C_{(2)}—N—H_{(N)}$	121(3)	$C_{(4)}—C_{(5)}—C_{(6)}$	111,0(5)	$C_{(5)}—C_{(6)}—C_{(17)}$	110,7(5)
$C_{(6)}—N—H_{(N)}$	115(3)	$C_{(4)}—C_{(5)}—H_{(5)}$	106(2)	$N_{(1)}—C_{(13)}—C_{(3)}$	175,7(8)
$N—C_{(2)}—C_{(3)}$	115,8(3)	$C_{(4)}—C_{(5)}—H_{(51)}$	114(2)	$N_{(2)}—C_{(14)}—C_{(15)}$	174,9(6)
$N—C_{(2)}—C_{(15)}$	121,4(5)	$C_{(6)}—C_{(5)}—H_{(5)}$	109(2)	$C_{(2)}—C_{(15)}—C_{(14)}$	124,5(5)
$C_{(3)}—C_{(2)}—C_{(15)}$	122,9(5)	$C_{(6)}—C_{(5)}—H_{(51)}$	108(3)	$C_{(2)}—C_{(15)}—C_{(16)}$	121,1(6)
$C_{(2)}—C_{(3)}—C_{(4)}$	120,2(5)	$H_{(5)}—C_{(5)}—H_{(51)}$	107(4)	$C_{(14)}—C_{(15)}—C_{(16)}$	114,2(5)
$C_{(2)}—C_{(3)}—C_{(13)}$	117,7(5)	$N—C_{(6)}—C_{(5)}$	105(2)	$N_{(3)}—C_{(16)}—C_{(15)}$	179,2(6)
$C_{(4)}—C_{(3)}—C_{(13)}$	121,8(5)	$N—C_{(6)}—C_{(17)}$	106,8(4)		



Conjugation of $N—C_{(2)}$ and $C_{(15)}—C_{(16)}$ with localization of the negative charge on the $N_{(3)}$ atom is most favorable, since $N_{(1)}\ldots N_{(2)}$ electrostatic repulsion increases in the case of localization of δ^- on $N_{(2)}$. This argument is confirmed by comparison of the $C_{(3)}—C_{(13)}$, $C_{(14)}—C_{(15)}$, and $C_{(15)}—C_{(16)}$ interatomic distances, the values of which decrease successively, and the negative charges (δ^-) on the $N_{(1)}$, $N_{(2)}$, and $N_{(3)}$ atoms should consequently change in the reverse order. The $C_{(2)}—C_{(3)}$ interatomic distance [1.472(7) Å] constitutes evidence for the absence of conjugation between the $N—C_{(2)}$ and $C_{(3)}—C_{(4)}$ and $C_{(3)}—C_{(13)}$ π fragments. The remaining interatomic distances are the ordinary ones and are in good agreement with the data in [7]. Thus the $C_{(4)}—C_{(7)}$ bond is shorter than the $C_{(4)}—C_{(5)}$ bond, since the first bond is formed by two atoms in the sp^2-hybrid state, while the $C_{(4)}—C_{(5)}$ bond is formed by one carbon atom in the sp^2 state and the other carbon atom in the sp^3 state. The single bond between carbon atoms in the sp^3 state is still longer.

The analysis of the conformation of the unsaturated heteroring of VIII is extremely interesting: the fragments that include the $C_{(6)}$, N, $C_{(2)}$, $C_{(3)}$ (A) and $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$ (B) atoms are planar in it. The deviation of the atoms from the root-mean-square value of the planes drawn through them does not exceed 0.002 Å for A, as compared with 0.017 Å for B. The deviations of the $C_{(4)}$ and $C_{(5)}$ atoms from plane A are 0.50 and 0.93 Å, while the deviations of the N and $C_{(6)}$ atoms from plane B are 0.43 and 0.92 Å, respectively. The angle between planes A and B is 21.9°. The optimal configuration, i.e., a virtually ideally skewed configuration of the σ bonds at the $C_{(5)}$ and $C_{(6)}$ atoms, is achieved for this conformation of the unsaturated heteroring of VIII. Thus torsion angle $H_{(5)}—C_{(5)}—C_{(6)}—C_{(23)} = 178°$, and angles $H_{(5)}—C_{(5)}—C_{(6)}—C_{(17)} = 52.7°$, $H_{(5)}—C_{(6)}—N = 63.3°$, and $H_{(51)}—C_{(5)}—C_{(6)}—N = 179.3°$.

The $C_{(5)}—H_{(5)}$ bond is virtually perpendicular to the $C_{(4)}—C_{(7)}$ bond (96.7°), while the $H_{(51)}$ atom deviates by 21° from the $C_{(4)}—C_{(7)}$ bond σ bond, which leads to repulsion of the $C_{(5)}—H_{(51)}$ σ bond from the $C_{(4)}—C_{(7)}$ σ bond; angle $C_{(4)}—C_{(5)}—H_{(51)} = 114(2)°$, while angle $C_{(4)}—C_{(5)}—H_{(5)} = 106(2)°$. The larger values of angles $C_{(4)}C_{(3)}—C_{(13)}$ and $C_{(3)}—C_{(4)}—C_{(7)}$ as compared with angles $C_{(2)}-C_{(3)}-C_{(13)}$ and $C_{(5)}-C_{(4)}-C_{(7)}$ (Table 3) also constitute evidence for repulsion of the $C_{(3)}-C_{(13)}$ and $C_{(4)}-C_{(7)}$ bonds [torsion angle $C_{(13)}-C_{(3)}-C_{(4)}-C_{(7)}$ = 11.5°].

As we have already noted, significant interaction occurs between the groups of $C_{(15)}-C_{(14)}-N_{(2)}$ and $C_{(3)}-C_{(13)}-N_{(1)}$ atoms; this leads to deviation of the $C_{(13)}$ (0.62 Å) and $N_{(1)}$ (1.19 Å) atoms from plane A.

Of the intermolecular contacts, one should note the rather short distance $N_{(3)}\cdots H_{(N)}$ (I–X, I–V, I–Z) = 2.36 Å.

EXPERIMENTAL

Light-yellow single crystals of VIII [2] were obtained by slow cooling of a solution of VIII in benzene–hexane (1:1). The unit cell parameters and the three-dimensional set of intensities were determined with an SAD-4 four-circle automatic diffractometer: a = 9.559(2), b = 10.400(2), c = 12.999(2) Å, α = 111.34(3)°, β = 100.82(3)°, γ = 83.57(2)°, Fedorov group P1, Z = 2. Molybdenum K_α emission, a graphite monochromator, and ω scanning were used. The structural motif was found by direct methods with the use of the MULTAN-83 program, which was realized in a complex of SDP programs.

Refinement of the position and heat parameters of the nonhomogeneous atoms was accomplished within an anisotropic total-matrix variant. The number of reflections in the method of least squares ($|F|^2 > 2\sigma$) was 1714. The final R factor was 0.047.

The x-ray diffraction experiment was carried out in the laboratory of structural chemistry of the chemistry department of Moscow State University.

LITERATURE CITED

1. D. W. M. Anderson, F. Bell, and J. L. Duncan, J. Chem. Soc., No. 11, 4705 (1961).
2. M. R. S. Weir and J. B. Hyne, Can. J. Chem., 43, 772 (1965).
3. Yu. T. Abramenko, Yu. A. Baskakov, Yu. A. Sharanin, A. F. Vasil'ev, E. B. Nazarova, N. A. Kiseleva, and O. N. Vlasov, Zh. Vsesoyuzn. Khim. Obshch., 24, 408 (1979).
4. Yu. T. Abramenko, A. V. Ivashchenko, K. A. Nogaeva, N. A. Andronova, and E. B. Putsykina, Zh. Org. Khim., 22, 264 (1986).
5. Yu. T. Abramenko, A. V. Ivashchenko, K. A. Nogaeva, and Yu. A. Sharanin, Khim. Geterotsikl. Soedin., No. 5, 621 (1986).
6. J. Mirek and P. Milart, Z. Naturforsch., 41b, 1471 (1986).
7. International Tables for X-Ray Crystallography, Vol. 3 (1962), p. 277.