STRUCTURE OF 4-AMINO-6-PHENYL-5-CYANO-2-CYCLOHEXANESPIRO-1,3-DITHIA-4-CYCLOHEXENE AND ITS RECYCLIZATION TO 5,6-TETRAMETHYLENE-4-PHENYL-3-CYANO-2[1H]PYRIDINETHIONE

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In our previous work [1], we showed that 4-amino-6-aryl-5-cyano-1,3-dithiacyclohexene-2-spirocycloalkanes recyclize to 4-aryl-5,6-polymethylene-3-cyanopyridine-2[1H]-thiones.\* In the present article, data related to the structure and chemical properties of the starting cyclohexenes indicating the mechanism for its recyclization are discussed in the case of the recyclization of 4-amino-6-phenyl-5-cyano-2-cyclohexanespiro-1,3-dithia-4-cyclohexane (I) t 4-phenyl-5,6-tetramethylene-3-cyanopyridine-2[1H]-thione (II).

The structure of (I) was determined by x-ray diffraction structural analysis (Fig. 1). The bond lengths are given in Table 1. The numbering of the atoms differs from the chemical scheme. The bond angles and several torsion angles are given in Table 2.

In the central six-membered heterocycle, S<sup>1</sup> and C<sup>1</sup> extrude from the plane of the four remaining atoms by -0.655 and 0.381 Å, respectively, † i.e., the heterocycle has deformed half-chair conformation which may be seen as intermediate between chair and twist boat. This is supported by the modified values [2] of the Cremer-Pople parameters [3] ( $q_2 = 0.511$  Å,  $q_2 = 247.8^{\circ}$ ,  $q_3 = 0.660$  Å, Q = 0.835 Å).

The S-C<sub>SP</sub><sup>3</sup> bond lengths differ. While the S<sup>1</sup>-C<sup>4</sup> bond length (1.811(5) Å) is very close to the standard S-C<sub>SP</sub><sup>3</sup> value (1.817(5) Å [4]), the S<sup>1</sup>-C<sup>1</sup> bond (1.801(4) Å) is less and S<sup>2</sup>-C<sup>1</sup> bond (1.825(5) Å) is longer than this value. The S<sup>2</sup>-C<sup>2</sup> bond length (1.749(5) Å) is somewhat shorter than the standard value for the S-C<sub>SP</sub><sup>2</sup> bond length (1.766(6) Å [5]).

Interest was found in the geometry of the planar fragment‡ of (I) involving the  $C^{2}=C^{3}$ double bond and attached atoms (Fig. 2). On one hand, this fragment has significant conjugation in the N<sup>1</sup>-C<sup>2</sup>=C<sup>3</sup>-C<sup>16</sup>=N<sup>2</sup> chain. Indeed, the coordination plane of the planar trigonal N<sup>1</sup> atom is almost coplanar with the plane of the S<sup>2</sup>C<sup>2</sup>C<sup>3</sup>C<sup>4</sup> fragment, which is favorable for the  $\pi$ -interaction of the unshared electron pair of N<sup>1</sup> with the  $\pi$ -system of the C<sup>2</sup>=C<sup>3</sup> bond. Secondly, the N<sup>1</sup>-C<sup>2</sup> bond length (1.349(7) Å) is reduced, the C<sup>2</sup>-C<sup>3</sup> bond length (1.374(6) Å) is increased, while the C<sup>3</sup>-C<sup>16</sup> bond length (1.412(7) Å) is also reduced relative to the standard values of the Nsp<sup>3</sup>-Csp<sup>2</sup>, Csp<sup>2</sup>=Csp<sup>2</sup>, and Csp<sup>2</sup>-Csp bond lengths which are 1.426(12) [6], 1.339[5], and 1.426(5) Å [4], respectively. On the other hand, the C<sup>16</sup>-N<sup>2</sup> bond length (1.145(7) Å) is close to the standard value for the C=N triple bond (1.157(5) Å [4]), i.e., it is not expanded.

The expansion of the  $C^2C^3C^4$  bond angle to  $128.1(4)^\circ$  may be attributed to the electronwithdrawing capacity of the CN group [7]. The expansion of the  $S^2C^2C^3$  intracyclic bond

\*The number of the atoms in this article is according to the IUPAC system while the numbering used in the discussion of the x-ray diffraction structural analysis is in accord with Fig. 1.  $+S^2$ ,  $C^2$ ,  $C^3$  and  $C^4$  extrude from the plane traversing them (-0.666x - 0.366y - 0.649z + 4.097 = 0) by 0.006, -0.016, 0.017, and -0.007 Å, respectively. The deviations of  $S^1$ ,  $C^1$ ,  $N^1$ ,  $N^2$ , and  $C^{16}$  from this plane are -0.655, 0.381, -0.082, 0.143, and 0.075 Å, respectively.  $\pm S^2$ ,  $C^2$ ,  $C^3$ ,  $C^4$ ,  $N^1$ ,  $C^{16}$ ,  $N^2$ ,  $H^1(N^1)$  and  $H^2(N^1)$  deviate from the plane traversing them (-0.645x - 0.405y - 0.648z + 4.046 = 0) by 0.073, 0.018, -0.009, -0.084, -0.007, 0.034, 0.089, 0.05, and -0.17 Å, respectively.

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Fig. 1. Molecular structure of (I).

TABLE 1. Bond Lengths in Structure (I)

Bond	<i>d</i> , A	Bond	d, Å
$\begin{array}{c} S^{1}-C^{1}\\ S^{1}-C^{4}\\ S^{2}-C^{1}\\ S^{2}-C^{2}\\ C^{1}-C^{5}\\ C^{1}-C^{9}\\ C^{2}-C^{3}\\ C^{2}-N^{1}\\ C^{3}-C^{4}\\ C^{3}-C^{16}\\ C^{4}-C^{10} \end{array}$	$\begin{array}{c} 1,801(4)\\ 1,811(5)\\ 1,825(5)\\ 1,749(5)\\ 1,538(7)\\ 1,536(7)\\ 1,374(6)\\ 1,349(7)\\ 1,513(6)\\ 1,412(7)\\ 1,522(6) \end{array}$	$\begin{array}{c} C^5-C^6\\ C^6-C^7\\ C^7-C^8\\ C^8-C^9\\ C^{10}-C^{11}\\ C^{10}-C^{15}\\ C^{11}-C^{12}\\ C^{12}-C^{13}\\ C^{13}-C^{14}\\ C^{14}-C^{15}\\ C^{16}-N^2 \end{array}$	$\begin{array}{c} 1,527(7)\\ 1,524(9)\\ 1,522(9)\\ 1,524(7)\\ 1,386(8)\\ 1,363(7)\\ 1,363(7)\\ 1,362(8)\\ 1,361(9)\\ 1,391(11)\\ 1,395(7)\\ 1,145(7)\end{array}$

angle to 126.9(4)° may be a consequence of requirements for closure of the ring containing a double bond. The sulfur bond angles fall within the rather broad range of values observed in six-membered rings [8].

The tendency of the NH<sub>2</sub> groups and the groups attached to the  $C^2=C^3$  double bond toward coplanarity as a result of their participation in a common conjugated system leads to short nonbonded contacts H<sup>2</sup>, N<sup>1</sup>···C<sup>16</sup> (2.48(1) Å) and N<sup>1</sup>···C<sup>16</sup> (2.717(6) Å) (the sum of the corresponding van der Waals radii is 2.90 and 3.25 Å, respectively [9]), which, in turn, leads to the large twisting about the  $C^2=C^3$  bonds (the N<sup>1</sup>C<sup>2</sup>C<sup>3</sup>C<sup>16</sup> torsion angle is 4.5(5)° and the twist about  $C^2-N^1$  is 9.2(4)°). The steric interaction of the H<sub>2</sub>N and CN groups is also seen in the expansion of the N<sup>1</sup>C<sup>2</sup>C<sup>3</sup> bond angle to 122.5(4)° and the extrusion of N<sup>1</sup> and C<sup>16</sup> in opposite directions from the double bond plane. Expansion of the C<sup>2</sup>C<sup>3</sup>C<sup>16</sup> bond angle (115.8(4)°) relative to the C<sup>4</sup>C<sup>3</sup>C<sup>16</sup> bond angle (116.1(4)°) is not observed since the CN group is also sterically hindered by the pseudoequatorial Ph group which is rotated relative to the S<sup>2</sup>C<sup>2</sup>C<sup>3</sup>C<sup>4</sup> plane by 69.1°. The C<sup>16</sup>···C<sup>10</sup> (2.877(7) Å) and C<sup>16</sup>···C<sup>11</sup> (3.166(7) Å) distances are less than twice the van der Waals radius of carbon (3.40 Å [9]), which leads to some expansion of the C<sup>3</sup>C<sup>4</sup>C<sup>10</sup> bond angle to 112.9(4)°. On the other hand, the C<sup>3</sup>-C<sup>4</sup> bond has a normal length (1.513(6) Å) (the standard value is 1.510(5) Å [4]) as in the case of the C<sup>4</sup>-C<sup>10</sup> bond which connects the Ph group to the heterocycle (1.522(6) Å) (the standard value is 1.52(1) Å [4]).

The cyclohexane ring spirofused with the heterocycle has chair conformation; the mean value of the torsion angles  $(54.2(1.7)^\circ)$  is close to that observed in compounds such as (III) (the mean values in rings A and B are 53.6° and 54.3°, respectively) [10]:





Fig. 2. Planar fragment of the heterocycle in (I) including the  $C^2=C^3$  double bond and attached atoms. The direction of the  $N^1-H^1(N^1)\cdots N^{2^*}$  intermolecular hydrogen bond is shown.



Fig. 3. The crystal structure of (I); the hydrogen bonds are indicated by dashed lines.

On the other hand, the marked flattening of the cyclohexane ring in (I) and approaching the spiro fragment (see Table 2) is less pronounced in (III) and may be a result of steric strain in (I). As in the case of ring B in (III), the C-C bond lengths in the spiro fragment in (I) (mean 1.537(7) Å) are somewhat greater than for the other C-C bonds in the cyclohexane ring (mean 1.524(4) Å). However, the mean value over the entire ring (1.528(7) Å) hardly differs from that observed in unsubstituted cyclohexane (1.535(2) Å [11]).

The N<sup>1</sup>-H<sup>1</sup>(N<sup>1</sup>)···N<sup>2</sup>' hydrogen bonds (N<sup>1</sup>···N<sup>2</sup>', 3.026(5) Å; N<sup>1</sup>···H<sup>1</sup>(N<sup>1</sup>), 0.91(6) Å; H<sup>1</sup>(N<sup>1</sup>)···N<sup>2</sup>', 2.13(5) Å, N<sup>1</sup>H<sup>1</sup>(N<sup>1</sup>)N<sup>2</sup>' 170.4(9)°) between the NH<sub>2</sub> group of one molecule and the CN group of another connects the molecules in the crystal of (I) into infinite helices along the 2<sub>1</sub> screw axes (the second hydrogen atom of the NH<sub>2</sub> group does not participate in hydrogen bonding) (Fig. 3). No other intermolecular distances less than the sums of the van der

Angle	ω	Angle	ω	Ang1e	τ
$\begin{array}{c} C^{1}S^{1}C^{4}\\ C^{1}S^{2}C^{2}\\ S^{1}C^{1}C^{5}\\ S^{1}C^{1}C^{5}\\ S^{2}C^{1}C^{5}\\ S^{2}C^{1}C^{5}\\ S^{2}C^{1}C^{5}\\ S^{2}C^{2}C^{3}\\ S^{2}C^{2}C^{3}\\ S^{2}C^{2}N^{4}\\ C^{3}C^{2}N^{4}\\ C^{2}C^{3}C^{1}6\\ S^{4}C^{3}C^{1}6\\ S^{1}C^{4}C^{3}\\ S^{1}C^{4}C^{1}0\\ \end{array}$	$\begin{array}{c} 101,0(2)\\ 1004,4(2)\\ 109,6(2)\\ 106,1(3)\\ 113,1(3)\\ 106,2(3)\\ 111,2(3)\\ 110,4(4)\\ 126,9(4)\\ 110,7(4)\\ 122,5(4)\\ 128,1(4)\\ 115,8(4)\\ 115,8(4)\\ 116,1(4)\\ 113,2(3)\\ 105,6(3)\\ \end{array}$	C <sup>3</sup> C <sup>4</sup> C <sup>10</sup> C <sup>1</sup> C <sup>5</sup> C <sup>6</sup> C <sup>6</sup> C <sup>7</sup> C <sup>8</sup> C <sup>7</sup> C <sup>8</sup> C <sup>9</sup> C <sup>1</sup> C <sup>10</sup> C <sup>15</sup> C <sup>4</sup> C <sup>10</sup> C <sup>15</sup> C <sup>11</sup> C <sup>11</sup> C <sup>15</sup> C <sup>11</sup> C <sup>11</sup> C <sup>12</sup> C <sup>11</sup> C <sup>12</sup> C <sup>13</sup> C <sup>11</sup> C <sup>12</sup> C <sup>13</sup> C <sup>14</sup> C <sup>12</sup> C <sup>13</sup> C <sup>14</sup> C <sup>13</sup> C <sup>14</sup> C <sup>15</sup> C <sup>10</sup> C <sup>15</sup> C <sup>14</sup>	$\begin{array}{c} 112.9(4)\\ 112.8(4)\\ 110,5(5)\\ 111,4(5)\\ 111,4(5)\\ 113,1(4)\\ 120,8(4)\\ 120,8(4)\\ 120,4(4)\\ 118,8(5)\\ 120,6(5)\\ 121,6(6)\\ 118,5(6)\\ 120,0(6)\\ 120,4(5)\\ 178,9(5)\\ \end{array}$	C <sup>1</sup> C <sup>5</sup> C <sup>6</sup> C <sup>7</sup> C <sup>5</sup> C <sup>6</sup> C <sup>7</sup> C <sup>8</sup> C <sup>9</sup> C <sup>7</sup> C <sup>8</sup> C <sup>9</sup> C <sup>1</sup> C <sup>8</sup> C <sup>9</sup> C <sup>1</sup> C <sup>5</sup> C <sup>9</sup> C <sup>1</sup> C <sup>5</sup> C <sup>9</sup> Mean	$\begin{array}{c} -55,8(6) \\ 56,4(6) \\ -55,4(6) \\ 53,3(6) \\ -51,3(5) \\ 52,9(5) \\ 54,2(1,7) \end{array}$

TABLE 2. Bond (  $\omega)$  and Torsion (  $\tau$  ) Angles in the Cyclohexane Ring, deg

Waals radii were found. The shortest carbon  $\cdot \cdot \cdot \cdot$  carbon intermolecular distance  $(C^{15} \cdot \cdot \cdot C^{15}, 3.407(8) \text{ Å})$  is equal to twice the carbon van der Waals radius (3.40 Å [9]). The intermolecular contacts less than 4 Å are given in Table 3.

The finding of a strong IR band at 2190 cm<sup>-1</sup> (conjugated C=N group) and of two PMR singlets at 5.0 and 5.1 ppm for the proton at C<sup>6</sup> (C<sup>4</sup> in Fig. 1) in the PMR spectra of dithiolenes with two different alkyl substituents at C<sup>2</sup> (C<sup>1</sup> in Fig. 1) also indicates conformational rigidity of the heterocycle in (I). For this reason, the introduction of external energy into dithiolene (I) apparently should lead to the opening of the heterocycle at the weakest S-C bond (S<sup>1</sup>-C<sup>6</sup> and S<sup>3</sup>-C<sup>2</sup>, i.e., S<sup>1</sup>-C<sup>4</sup> and S<sup>2</sup>-C<sup>1</sup> in Fig. 1) with the formation of cyclo-hexanethione (V) and benzylidenecyanothioacetamide (IV) (see scheme below). Bond redistribution occurs in the conjugated fragment in (I) (the C<sup>4</sup>-C<sup>5</sup> bond and its environment)



Only thicketone (V) was isolated upon the thermal decomposition of (I) [12]. Benzylidenecyanothicacetamide (IV) could not be isolated, apparently due to the ready dimerization of this compound and its derivatives [13]. However, the existence of (IV) is indicated by the formation of thiazole (XI) upon the addition of phenacyl bromide into the reaction mixture. Thiazole (XI) was also obtained independently from (XII) according to Schefer and Gewald [14].

Distance d		Distance	d	
$\begin{array}{c} \mathrm{S}^{1} \dots \mathrm{C}^{5}(\mathrm{I}) \\ \mathrm{S}^{4} \dots \mathrm{C}^{12}(\mathrm{II}) \\ \mathrm{S}^{2} \dots \mathrm{C}^{5}(\mathrm{II}) \\ \mathrm{C}^{2} \dots \mathrm{C}^{9}(\mathrm{III}) \\ \mathrm{C}^{3} \dots \mathrm{C}^{9}(\mathrm{III}) \\ \mathrm{C}^{5} \dots \mathrm{C}^{15}(\mathrm{I}) \\ \mathrm{C}^{6} \dots \mathrm{C}^{14}(\mathrm{I}) \\ \mathrm{C}^{6} \dots \mathrm{C}^{15}(\mathrm{I}) \\ \mathrm{C}^{7} \dots \mathrm{C}^{14}(\mathrm{V}) \\ \mathrm{C}^{7} \dots \mathrm{C}^{14}(\mathrm{I}) \\ \mathrm{C}^{8} \dots \mathrm{V}^{1}(\mathrm{II}) \end{array}$	3,981 (5) 3,784 (6) 3,838 (6) 3,933 (7) 3,944 (7) 3,952 (7) 3,934 (8) 3,877 (10) 3,786 (8) 3,943 (9) 3,965 (10) 3,942 (8)	$ \begin{array}{c} C^9 \ldots C^{16}  (III) \\ C^9 \ldots N^4  (III) \\ C^{11} \ldots C^{12}  (II) \\ C^{11} \ldots C^{12}  (II) \\ C^{11} \ldots N^4  (IV) \\ C^{12} \ldots N^4  (IV) \\ C^{13} \ldots N^4  (IV) \\ C^{14} \ldots C^{15}  (III) \\ C^{14} \ldots C^{15}  (III) \\ C^{15} \ldots C^{15}  (III) \\ C^{16} \ldots N^1  (IV) \end{array} $	$\begin{array}{c} 3,826\ (7)\\ 3,934\ (7)\\ 3,933\ (8)\\ 3,769\ (8)\\ 3,815\ (8)\\ 3,815\ (8)\\ 3,817\ (9)\\ 3,797\ (10)\\ 3,841\ (9)\\ 3,407\ (8)\\ 3,754\ (6) \end{array}$	

TABLE 3. Shortest Intermolecular Contacts (d, Å) Between Non-Hydrogen Atoms in the Crystal\* (<4 Å)

\*Symmetry relationships: (I).  $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$ ; (II).  $\bar{x} + \frac{1}{2}$ ,  $\bar{y} + \frac{1}{2}$ ,  $\bar{z}$ ; (III).  $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z} + \frac{1}{2}$ ; (IV).  $\bar{x} + \frac{1}{2}$ ,  $\frac{1}{2} + y$ ,  $\bar{z} + \frac{1}{2}$ ; (V).  $x + \frac{1}{2}$ ,  $y + \frac{1}{2}$ , z.



For a more detailed understanding of the mechanism for the recyclization of (I), we studied the reaction of cyclohexanethione (V) and benzylidenecyanothioacetamide (IV) in methanol in the presence of morpholine at about 25°C leading to the formation of (II) in 78% yield. We may assume that under Michael reaction conditions, (V) adds to (IV) with the formation of an adduct (VI)  $\neq$  (VII). The elimination of H<sub>2</sub>S leads to dihydropyridine-thione (VIII), which is readily oxidized under the reaction conditions to final product (II). However, the presence of morpholine may lead initially to the formation of enamine (X) from thioketone (V), while the subsequent reaction of (X) with (V) leads to adduct (VI). This assumption was supported experimentally since the condensation of (IV) and (X) leads to the formation of pyridinethione (II).

Also, cyclohexanone (IX) reacts with (IV) in the presence of morpholine to form (II). This reaction, in our opinion, is a convenient method for the synthesis of 2(1H)-pyridine-thiones.

## EXPERIMENTAL

The unit cell parameters of colorless, monoclinic crystals of (I) at 20°C were: a = 15.283(2), b = 11.6878(7), c. = 18.317(1) Å,  $\beta = 105.373(6)^{\circ}$ , V = 3154.7(7) Å<sup>3</sup>, d<sub>calc</sub> = 1.2742 g/cm<sup>3</sup>, Z = 8, C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>, space group C<sub>2/C</sub>. The intensities of 2776 reflection were taken on a Hilger-Watts automatic four-circle diffractometer using  $\lambda$ CuK<sub> $\alpha$ </sub> radiation, graphite monochromator,  $\theta/2\theta$  scanning to  $\theta_{max} = 66^{\circ}$ . The structure was solved by the Patterson method and refined by full-matrix method of least squares in the anisotropic approximation for the non-hydrogen atoms for 2495 reflections with I  $\geq 2\sigma$ . The hydrogen atoms were objectively located in the difference map and refined with fixed B<sub>iso</sub> = 5 Å<sup>2</sup>. The final R value was 0.066 (R<sub>W</sub> = 0.090). All the calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [15]. The coordinates and isotropic equivalent temperature parameters of the atoms are given in Table 4.

The IR spectra were taken for KBr pellets on a Perkin-Elmer 457 spectrometer. The PMR spectra were taken on a Varian FT-80A spectrometer at 80 MHz for solutions in DMSO- $d_6$  with TMS as the internal standard.

Thin-layer chromatography was used to monitor the course of the reactions and purity of the compounds using Silufol UV-254 plates with 3:5 acetone-hexane as eluent.

Atom	x	) Y	z	Atom	x	Ŷ	z
$ \begin{array}{c} S^{1} \\ S^{2} \\ C^{2} \\ C^{3} \\ C^{5} \\ C^{6} \\ C^{7} \\ C^{8} \\ C^{10} \\ C^{11} \\ C^{12} \\ C^{13} \\ C^{14} \\ C^{15} \\ C^{16} \\ N^{1} \\ N^{2} \end{array} $	$\begin{array}{c} 10328 (8) \\ 17135 (9) \\ 804 (3) \\ 1876 (3) \\ 1507 (3) \\ 926 (3) \\ 859 (3) \\ 611 (4) \\ -330 (4) \\ -391 (4) \\ -391 (4) \\ -391 (4) \\ 2254 (3) \\ 2049 (4) \\ 2254 (4) \\ 1601 (5) \\ 703 (5) \\ 489 (4) \\ 1699 (3) \\ 2438 (3) \\ 484 (2) \\ \end{array}$	$\left \begin{array}{c} 475(10)\\ -20764(11)\\ -1448(4)\\ -1106(4)\\ -31(4)\\ 601(4)\\ -3288(4)\\ -3288(4)\\ -3453(5)\\ -2929(4)\\ -3453(5)\\ -2929(4)\\ 1867(4)\\ 2224(4)\\ 3558(5)\\ 4177(5)\\ 3833(5)\\ 2677(4)\\ 557(4)\\ -1548(4)\\ -1548(4)\\ -027(6)\end{array}\right $	$\begin{array}{c} 44709(7)\\ 39297(8)\\ 4273(2)\\ 3251(3)\\ 3108(3)\\ 5040(3)\\ 4966(3)\\ 4429(4)\\ 3656(4)\\ 3718(3)\\ 3631(3)\\ 3996(3)\\ 3996(3)\\ 3800(4)\\ 3524(4)\\ 3524(4)\\ 3524(4)\\ 3524(4)\\ 3451(3)\\ 2495(3)\\ 2866(3)\\ 1990(3)\\ \end{array}$	$H^{1}N^{4}$ $H^{2}N^{1}$ $H^{4-}$ $H^{5,1}$ $H^{6,1}$ $H^{6,2}$ $H^{7,1}$ $H^{8,1}$ $H^{8,1}$ $H^{9,1}$ $H^{9,1}$ $H^{12}$ $H^{11}$ $H^{12}$ $H^{13}$ $H^{14}$ $H^{15}$	$\begin{array}{c} 270(4)\\ 264(4)\\ 29(3)\\ 43(3)\\ 156(4)\\ 71(4)\\ 111(4)\\ -73(4)\\ -52(3)\\ -92(4)\\ 0(3)\\ -16(3)\\ 246(4)\\ 289(4)\\ 177(4)\\ 24(4)\\ -11(4) \end{array}$	$\begin{array}{c} -225(5)\\ -119(5)\\ 54(4)\\ -156(4)\\ -195(5)\\ -365(5)\\ -364(5)\\ -307(5)\\ -307(5)\\ -430(4)\\ -226(4)\\ -228(4)\\ -126(4)\\ -126(4)\\ 159(5)\\ 363(5)\\ 495(5)\\ -436(5)\\ 246(5)\end{array}$	$\begin{array}{c} 288 (3) \\ 261 (3) \\ 323 (3) \\ 524 (2) \\ 556 (3) \\ 488 (3) \\ 470 (3) \\ 427 (3) \\ 343 (3) \\ 342 (3) \\ 326 (3) \\ 326 (3) \\ 408 (3) \\ 419 (4) \\ 388 (3) \\ 338 (3) \\ 338 (3) \\ 328 (3) \\ 328 (3) \end{array}$

TABLE 4. Atomic Coordinates ( $\cdot 10^5$  for S Atoms,  $\cdot 10^4$  for N and C Atoms and  $\cdot 10^3$  for H Atoms)\*

\*The isotropic temperature factors may be obtained from the authors.

5,6-Tetramethylene-4-phenyl-3-cyano-2(1H)-pyridinethione (II). a) A suspension of 10 mmoles benzylidenecyanothioacetamide (IV) and 14 mmoles cyclohexanethione (V) in 20 ml abs. methanol in the presence of 1 ml morpholine was stirred for 8 h. A clear solution was formed from which the product crystallized out. The precipitate was filtered off and washed with ethanol and hexane. Recrystallization from acetic acid gave 2.07 g (78%) (II) mp 268-270° (dec.).

b) A mixture of 10 mmoles (IV) and 10 mmoles N-(cyclohexen-l-yl)morpholine:(X) in 20 ml methanol was stirred at 20-25°C for 10 h and the precipitate was separated to yield 2.3 g (86%) (II), mp 268-270°C.

c) A mixture of 10 mmoles (IV), 15 mmoles cyclohexanone and 1 ml morpholine in 20 ml abs. methanol was stirred at 25°C for 12 h and the precipitate was separated to give 2.1 g (83%) (II), mp 268-270°C. The samples obtained by methods a, b, and c were identical to the sample of (II) obtained according to our previous procedure [1].

<u>1-(4-Phenylthiazol-2-yl)-2-phenyl-1-cyanoethylene (XI)</u>. A sample of 10 mmoles (I) was heated at reflux in 35 ml methanol for 10-15 min and then 10 mmoles phenacyl bromide was added and reflux was continued for an additional 1 h. The reaction mixture was cooled and the precipitate was filtered off and washed with ethanol and hexane. The yield of (XI) after recrystallization from ethanol was 2.28 g (79%), mp 123-124°C. IR spectrum (KBr): v(CN) 2227 cm<sup>-1</sup>. PMR spectrum ( $\delta$ , ppm): 8.31 s (1H, thiazole CH), 8.23 s (1H, ethylene CH). Found: C, 74.81; H, 4.05; N, 9.76; S, 10.89%. Calculated for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>S: C, 74.97; H, 4.20; N, 9.71; S, 11.12%. The sample of (XI) did not give a depressed melting point with 1-(4-phenylthiazol-2-yl)-2-phenyl-1-cyanoethylene prepared according to Schefer [14].

## CONCLUSIONS

An intramolecular conformationally-rigid conjugation system was found in 4-amino-6phenyl-5-cyano-2-cyclohexanespiro-1,3-dithia-4-cyclohexene. A probable mechanism for recyclization to the corresponding 2(1H)-pyridinethione was proposed on the basis of the geometrical parameters.

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MOLECULAR STRUCTURE OF DIBENZOMETHYLPHOSPHONYL-2-CROWN-7

IN THE CRYSTALLINE STATE AND IN SOLUTION

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In previous communications, we presented the results of studies on dibenzomethylphosphonyl-14-crown-5, dibenzomethylthiophosphonyl-14-crown-5 [1] and dibenzoadamantylphosphonyl-17-crown-6 [2]. We concluded that these compounds in the crystalline phase and in solution exist in a conformation, in which the orientation of the unshared electron pairs of the donor atoms excludes cooperative bonding with the acceptor. The ethereal oxygen atoms in the phosphoryl and thiophosphoryl groups do not have marked electron-donor properties and thus are not effective coordination sites [3]. The number of actual electron-donor sites in these molecules does not exceed five, i.e., is less than the usual coordination number of calcium and magnesium. The introduction of a bulky adamantyl group in dibenzoadamantylphosphonyl-17-crown-6 leads to complexation with  $KNO_3$  and the exclusion of the ethereal oxygen atoms, which have considerable electron-donor properties, from interaction.

In the present work, we studied the structure of dibenzomethylphosphonyl-20-crown-7 (I) in the crystalline state and in solution using x-ray diffraction structural analysis, IR spectroscopy, dipole moment measurements and calculation of the nonbonding interactions. In comparison with the previously studied molecules, the number of effective donor sites, without taking account of the ethereal oxygen atoms at phosphorus, is equal to six. The size of the macrocyclic cavity is also greater.

## EXPERIMENTAL

Crown ether (I),  $C_{21}H_{27}PO_8$  was obtained according to Kirsanov et al. [4] as transparent, colorless needles. The unit cell parameters for these crystals were obtained on an RKOP camera and refined on a DRON-1 diffractometer using  $\lambda CuK_{\alpha}$  radiation: a = 23.907(6), b = 16.930(4), c = 5.356(1) Å,  $\beta = 100.33(5)^{\circ}$ , V = 2132.7 Å<sup>3</sup>, M = 438.2,  $d_{calc} = 1.36$  g/cm<sup>3</sup> for Z = 4.

The intensities of 955 independent nonzero reflections with I >  $2\sigma$  in the range of  $2\theta$  from 3° to 80° were measured on a DAR-UM diffractometer using CuK<sub> $\alpha$ </sub> radiation and a monochromator according to our previous procedure [5]. The observed extinctions unequivocally

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