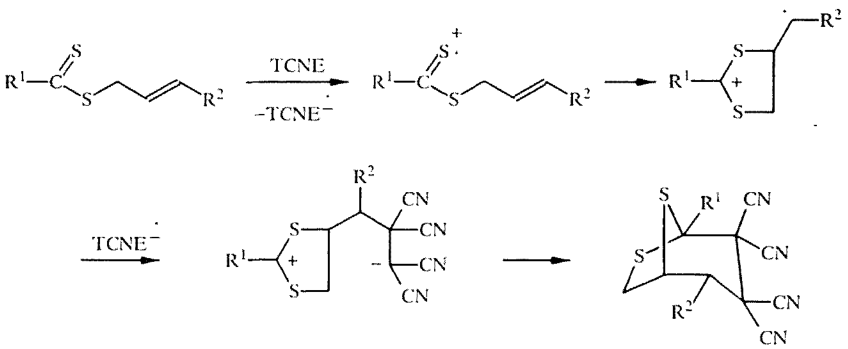
Chemistry of Heterocyclic Compounds, Vol. 30, No. 6, 1994

2,2,3,3-TETRACYANO-7,8-DITHIABICYCLO[3.2.1]OCTANES: STRUCTURAL STUDIES

I. V. Magedov, S. Yu. Shapakin, V. N. Drozd,
A. S. Batsanov, D. S. Yufit, and Yu. T. Struchkov

2,2,3,3-Tetracyano-7,8-dithiabicyclo[3.2.1]octanes were formed in the reaction of dithiocarboxylic acid allyl and cinnamyl esters with tetracyanoethylene, and their structure was determined by a number of physicochemical methods, including a x-ray structural study.

We recently discovered a new reaction of dithiocarboxylic acid allyl esters with tetracyanoethylene (TCNE) which yields 2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octanes [1].



I-III

I $R^1 = Ph$, $R^2 = H$; II $R^1 = R^2 = Ph$; III $R^1 = PhCH_2$, $R^2 = Ph$

The structure of reference compounds I-III was unambiguously determined with the data from the x-ray structural studies reported in the present article. The study of the structure of these compounds with other calculation and physicochemical methods, molecular mechanics and spectral methods in particular, especially with ^1H and ^{13}C NMR spectroscopy, will allow using the data obtained for determining the structure and conformations of other compounds of this class.

The overall form of molecules I-III is shown in Figs. 1-3, and the bond lengths and valence angles (experimental and calculated by the method of molecular mechanics) are reported in Tables 1 and 2.

The six-member thiacyclohexane ring in the 7,8-dithiabicyclo[3.2.1]octane skeleton of molecules I-III has an asymmetric chair conformation with inflection from the $C_{(1)}C_{(2)}C_{(4)}C_{(5)}$ plane along lines $C_{(1)}...C_{(5)}$ and $C_{(2)}...C_{(4)}$ by 63, 64, 64.4° and 39.9, 45, and 40.4°, respectively, with a precision of 0.01 Å, and $C_{(9)}N_{(9)}$ and $C_{(12)}N_{(12)}$ cyano groups are in the equatorial position, while $C_{(10)}N_{(10)}$ and $C_{(11)}N_{(11)}$ groups are in axial positions.

The five-member ring has a conformation intermediate between envelope with bending of the $S_{(8)}$ atom and half-chair: the $S_{(8)}$ and $C_{(5)}$ atoms deviate from the plane of the other three $C_{(1)}S_{(7)}C_{(6)}$ atoms by 0.796 and −0.214 Å, 0.86 and −0.20 Å, and 0.735 and −0.292 Å, respectively, for molecules I-III. For this reason, the conformation of the seven-member ring can be described as a distorted bath with a bend along lines $C_{(1)}...C_{(5)}$ and $C_{(2)}...C_{(4)}$.

K. A. Timiryazev Agricultural Academy, Moscow 127550. A. N. Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 770-780, June, 1994. Original article submitted May 18, 1994.

0009-3122/94/3006-0674$12.50

TABLE 1. Bond Lengths (Å) in Structures I-III

Bond	Experimental			Calculated		
	I	II	III	I	II	III
$S_{(7)}$—$C_{(1)}$	1,826(2)	1,817(4)	1,811(2)	1,833	1,828	1,833
$S_{(7)}$—$C_{(6)}$	1,832(3)	1,822(4)	1,817(3)	1,825	1,822	1,825
$S_{(8)}$—$C_{(1)}$	1,813(2)	1,814(4)	1,803(2)	1,832	1,829	1,832
$S_{(8)}$—$C_{(5)}$	1,819(3)	1,823(3)	1,818(2)	1,821	1,829	1,832
$N_{(9)}$—$C_{(9)}$	1,134(3)	1,138(6)	1,130(3)	1,166	1,166	1,166
$N_{(10)}$—$C_{(10)}$	1,135(3)	1,125(5)	1,132(2)	1,166	1,166	1,166
$N_{(11)}$—$C_{(11)}$	1,133(3)	1,123(5)	1,130(3)	1,166	1,166	1,166
$N_{(12)}$—$C_{(12)}$	1,133(3)	1,138(6)	1,132(3)	1,165	1,166	1,166
$C_{(1)}$—$C_{(2)}$	1,607(3)	1,610(6)	1,585(3)	1,566	1,564	1,568
$C_{(1)}$—$C_{(13)}$	1,516(3)	1,528(5)	—	1,523	1,524	—
$C_{(1)}$—$C_{(25)}$	—	—	1,545(3)	—	—	1,550
$C_{(2)}$—$C_{(3)}$	1,603(3)	1,599(4)	1,604(2)	1,572	1,576	1,582
$C_{(2)}$—$C_{(9)}$	1,483(3)	1,479(5)	1,483(3)	1,489	1,490	1,487
$C_{(2)}$—$C_{(10)}$	1,483(3)	1,482(5)	1,481(2)	1,489	1,487	1,491
$C_{(3)}$—$C_{(4)}$	1,557(3)	1,568(5)	1,571(3)	1,546	1,550	1,551
$C_{(3)}$—$C_{(11)}$	1,493(3)	1,506(5)	1,481(2)	1,488	1,485	1,487
$C_{(3)}$—$C_{(12)}$	1,492(3)	1,484(5)	1,481(3)	1,490	1,489	1,491
$C_{(4)}$—$C_{(5)}$	1,531(3)	1,537(5)	1,532(3)	1,542	1,548	1,550
$C_{(4)}$—$C_{(19)}$	—	1,520(4)	1,525(2)	—	1,523	1,522
$C_{(5)}$—$C_{(6)}$	1,515(4)	1,532(5)	1,519(3)	1,537	1,538	1,542
$C_{(13)}$—$C_{(14)}$	1,396(3)	1,387(6)	1,370(3)			
$C_{(13)}$—$C_{(18)}$	1,396(3)	1,399(6)	1,371(3)			
$C_{(13)}$—$C_{(25)}$	—	—	1,506(3)			1,511
$C_{(14)}$—$C_{(15)}$	1,380(4)	1,390(6)	1,387(5)			
$C_{(15)}$—$C_{(16)}$	1,375(4)	1,375(7)	1,355(5)			
$C_{(16)}$—$C_{(17)}$	1,381(4)	1,364(8)	1,350(5)			
$C_{(17)}$—$C_{(18)}$	1,383(3)	1,403(6)	1,375(4)			
$C_{(19)}$—$C_{(20)}$	—	1,386(6)	1,380(3)			
$C_{(19)}$—$C_{(24)}$	—	1,381(6)	1,372(3)			
$C_{(20)}$—$C_{(21)}$	—	1,387(6)	1,386(3)			
$C_{(21)}$—$C_{(22)}$	—	1,356(8)	1,360(3)			
$C_{(22)}$—$C_{(23)}$	—	1,382(7)	1,358(4)			
$C_{(23)}$—$C_{(24)}$	—	1,383(6)	1,384(3)			

Establishing the configuration of the position of the substituent (phenyl) in position 4 of compounds II and III was a very important consequence of the x-ray structural study: on the whole, as should have been predicted, it occupies the most advantageous equatorial position in the thiacyclohexane ring and consequently has an *endo* configuration.

The $C_{(1)}$—$S_{(8)}$ and $C_{(5)}$—$S_{(8)}$ bond lengths in bicycle I are close to the standard value of 1.817 Å for bonds of the S—C(sp^3) type [2], while the $C_{(1)}$—$S_{(7)}$ and $C_{(6)}$—$S_{(7)}$ bond lengths are lengthened slightly. Such inequality for these bonds is not unusual in skeleton compounds and has been observed in derivatives of 3,6,7-trithiabicyclo[2.2.1]heptane [3], 7-thia-2,3,8-triazabicyclo[3.2.1]octane [4], and 6,8-dioxa-3-thiabicyclo[3.2.1]octane, for example [5]. On the other hand, the lengths of these bonds in structure II are more equalized and their average value (1.817 Å) is almost the same as the standard value; on the contrary, the $C_{(1)}$—$S_{(7)}$ and $C_{(1)}$—$S_{(8)}$ bonds are shortened in structure III.

The lengths of the C—C bonds in the skeleton, according to the usual rules [2], increase symbatically to the number of substituents. The significant lengthening of $C_{(1)}$—$C_{(2)}$ bonds [1.607 (3) and 1.610(6) Å] in bicycles I and II in comparison to the average length of the bond between tertiary carbon atoms (1.588 Å) [2] could be due not only to steric repulsion of the substituents at the $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ atoms, but also to the electron-acceptor character of the cyano groups and the effective shift of the electron density from C(sp^3)—C(sp^3) bonds to C(sp^3)—CN bonds, whose multiplicity is increased. Such redistribution of the electron density obviously results in the fact that no absorption bands are observed in the IR spectra in the region of 2150-2300 cm^{-1} characterizing stretching vibrations of $C\equiv N$ bonds. However, not only electronic but also steric factors probably cause shortening of the $C_{(1)}$—$C_{(2)}$ bond [1.585(3) Å] in bicycle III in comparison to the two preceding structures, since the phenyl group at the nodal $C_{(1)}$ atom is substituted by a benzyl group, which has lower steric requirements, while the $C_{(2)}$—$C_{(3)}$ bond length is virtually preserved [1.604(2) Å].

TABLE 2. Valence Angles (°) in Molecules I-III

Angle	Experimental			Calculated		
	I	II	III	I	II	III
$C_{(1)}-S_{(7)}-C_{(6)}$	96,3(1)	95,6(2)	96,2(1)	98,3	98,2	97,2
$C_{(1)}-S_{(8)}-C_{(5)}$	90,2(1)	90,2(2)	90,1(1)	92,0	92,4	91,8
$S_{(7)}-C_{(1)}-S_{(8)}$	106,6(1)	106,8(2)	107,3(1)	102,9	101,9	103,9
$S_{(7)}-C_{(1)}-C_{(2)}$	107,7(1)	109,4(2)	108,2(1)	110,7	111,1	109,3
$S_{(8)}-C_{(1)}-C_{(2)}$	109,0(1)	107,7(2)	108,4(1)	109,6	109,9	109,6
$S_{(7)}-C_{(1)}-C_{(13)}$	112,5(1)	110,9(2)		111,3	110,8	
$S_{(8)}-C_{(1)}-C_{(13)}$	110,8(1)	112,7(3)		110,9	111,8	
$C_{(2)}-C_{(1)}-C_{(13)}$	110,0(2)	109,2(3)		111,2	111,1	
$S_{(7)}-C_{(1)}-C_{(25)}$			111,2(1)			107,6
$S_{(8)}-C_{(1)}-C_{(25)}$			112,1(1)			110,7
$C_{(2)}-C_{(1)}-C_{(25)}$			109,5(2)			115,1
$C_{(1)}-C_{(2)}-C_{(3)}$	113,7(1)	113,4(3)	114,0(2)	115,0	115,4	115,2
$C_{(1)}-C_{(2)}-C_{(9)}$	109,8(2)	111,5(3)	109,7(1)	109,9	108,1	109,7
$C_{(3)}-C_{(2)}-C_{(9)}$	108,0(2)	106,8(3)	108,5(1)	109,2	109,1	109,1
$C_{(1)}-C_{(2)}-C_{(10)}$	108,7(2)	107,9(3)	108,9(1)	108,3	109,7	109,0
$C_{(3)}-C_{(2)}-C_{(10)}$	108,2(2)	108,7(3)	108,0(1)	109,0	109,3	107,4
$C_{(9)}-C_{(2)}-C_{(10)}$	108,3(2)	108,4(3)	107,6(2)	104,9	104,7	105,9
$C_{(2)}-C_{(3)}-C_{(4)}$	112,9(2)	112,4(3)	112,9(2)	113,3	112,3	111,5
$C_{(2)}-C_{(3)}-C_{(11)}$	112,0(2)	111,9(3)	112,2(1)	112,7	111,8	113,5
$C_{(4)}-C_{(3)}-C_{(11)}$	110,4(2)	112,0(3)	111,3(2)	108,7	111,2	111,1
$C_{(2)}-C_{(3)}-C_{(12)}$	108,6(2)	106,6(3)	107,0(2)	110,8	109,9	109,9
$C_{(4)}-C_{(3)}-C_{(12)}$	108,7(2)	109,8(3)	107,9(1)	107,5	108,0	108,2
$C_{(11)}-C_{(3)}-C_{(12)}$	103,8(2)	103,5(3)	105,1(2)	103,1	103,1	102,7
$C_{(3)}-C_{(4)}-C_{(5)}$	114,4(2)	111,2(3)	112,9(1)	117,0	115,7	115,6
$C_{(3)}-C_{(4)}-C_{(19)}$		111,5(3)	111,7(2)		113,4	112,8
$C_{(5)}-C_{(4)}-C_{(19)}$		116,3(3)	116,3(2)		114,2	115,0
$S_{(8)}-C_{(5)}-C_{(4)}$	109,9(2)	109,4(3)	109,3(1)	107,4	107,0	106,4
$S_{(8)}-C_{(5)}-C_{(6)}$	106,7(2)	104,9(2)	105,2(1)	106,0	103,2	103,5
$C_{(4)}-C_{(5)}-C_{(6)}$	116,1(2)	119,1(3)	119,4(2)	114,7	118,2	118,5
$S_{(7)}-C_{(6)}-C_{(5)}$	109,3(2)	110,7(3)	109,4(2)	109,4	110,1	110,4
$N_{(9)}-C_{(9)}-C_{(2)}$	178,2(2)	175,7(4)	179,1(2)	179,0	179,0	179,6
$N_{(10)}-C_{(10)}-C_{(2)}$	179,7(3)	179,0(4)	179,1(2)	178,6	178,3	177,3
$N_{(11)}-C_{(11)}-C_{(3)}$	171,3(2)	171,4(4)	171,6(2)	178,2	179,4	178,6
$N_{(12)}-C_{(12)}-C_{(3)}$	178,3(2)	178,0(4)	177,5(2)	179,3	179,1	179,3
$C_{(1)}-C_{(13)}-C_{(14)}$	121,2(2)	120,5(3)				
$C_{(1)}-C_{(13)}-C_{(18)}$	120,8(2)	120,2(3)				
$C_{(14)}-C_{(13)}-C_{(18)}$	118,0(2)	119,3(3)	118,3(2)			
$C_{(14)}-C_{(13)}-C_{(25)}$			121,0(2)			
$C_{(18)}-C_{(13)}-C_{(25)}$			120,7(2)			
$C_{(13)}-C_{(14)}-C_{(15)}$	120,5(2)	120,5(4)	120,3(2)			
$C_{(14)}-C_{(15)}-C_{(16)}$	120,8(2)	120,2(5)	120,1(3)			
$C_{(15)}-C_{(16)}-C_{(17)}$	119,7(2)	119,9(4)	120,1(3)			
$C_{(16)}-C_{(17)}-C_{(18)}$	119,9(2)	121,2(5)	120,1(3)			
$C_{(13)}-C_{(18)}-C_{(17)}$	121,1(2)	118,8(4)	121,0(2)			
$C_{(4)}-C_{(19)}-C_{(20)}$		123,8(3)	124,7(2)			
$C_{(4)}-C_{(19)}-C_{(24)}$		119,1(3)	117,6(2)			
$C_{(20)}-C_{(19)}-C_{(24)}$		117,1(3)	117,7(2)			
$C_{(19)}-C_{(20)}-C_{(21)}$		121,1(5)	120,9(2)			
$C_{(20)}-C_{(21)}-C_{(22)}$		120,9(5)	120,4(2)			
$C_{(21)}-C_{(22)}-C_{(23)}$		119,2(4)	119,3(2)			
$C_{(22)}-C_{(23)}-C_{(24)}$		119,8(5)	120,7(2)			
$C_{(19)}-C_{(24)}-C_{(23)}$		121,9(4)	121,0(2)			
$C_{(1)}-C_{(25)}-C_{(13)}$			114,5(2)			117,5

The pronounced kink of the axial cyano group at the $C_{(3)}$ atom is an interesting feature of compounds II and III: the angle of $C_{(3)}C_{(11)}N_{(11)}$ is equal to 171.4±0.2°, undoubtedly caused by the two short intramolecular 1,3-biaxial contacts in the chair-like thiacyclohexane ring between this cyano group and the $S_{(7)}$—$C_{(6)}$ bridge (for example, the $S_{(7)}...C_{(11)}$ distance for compound I is equal to 3.024(3) Å, and the $C_{(6)}...C_{(11)}$ distance is 3.099(4) Å).

The same interactions decrease the valence angle between the geminal cyano groups at the $C_{(3)}$ atom: 103.8(2), 103.5(3), and 105.1(2)° for compounds I-III, respectively, while the same angle at the $C_{(2)}$ atom is practically equal to 108°. The $C_{(2)}C_{(3)}C_{(11)}$ angle increases to approximately 112°, and the $C_{(4)}C_{(3)}C_{(11)}$ angle increases to 110.5-112°; the $C_{(2)}C_{(3)}C_{(12)}$ and $C_{(4)}C_{(3)}C_{(12)}$ angles are virtually not deformed.

TABLE 3. Experimental (θ_{expt}) and Calculated (θ_{calc}) Torsional Angles, Vicinal SSCC Calculated with the Karplus Equation for the Corresponding Angles Determined by XSA (^3J_X, Hz) or Molecular Mechanics (^3J_M, Hz), and the SSCC Measured with the PMR Spectra of Compounds I-III ($^3J_{PMR}$, Hz)

Compound	Torsional angle	θ_{expt}	^3J_X	θ_{calc}	^3J_M	$^3J_{PMR}$
I	$H_{(4a)}—C_{(4)}—C_{(5)}—H_{5)}$	-59,20	3,15	-61,50	2,54	4,0
	$H_{(4b)}—C_{(4)}—C_{(5)}—H_{(5)}$	59,50	2,85	51,84	4,47	2,9
	$H_{(6a)}—C_{(4)}—C_{(5)}—H_{(5)}$	37,50	6,59	38,06	6,51	5,6
	$H_{(6b)}—C_{(4)}—C_{(5)}—H_{(5)}$	-88,20	0,93	-78,85	1,03	—
II	$H_{(4a)}—C_{(4)}—C_{(5)}—H_{(5)}$	-72,90	1,04	-72,31	1,14	1,8
	$H_{(6a)}—C_{(4)}—C_{(5)}—H_{(5)}$	34,80	7,20	38,86	6,38	5,5
	$H_{(6b)}—C_{(4)}—C_{(5)}—H_{(5)}$	-83,50	0,91	-77,85	1,07	0,6
III	$H_{(4a)}—C_{(4)}—C_{(5)}—H_{(5)}$	-69,20	1,43	-72,96	1,02	—
	$H_{(6a)}—C_{(4)}—C_{(5)}—H_{(5)}$	38,00	6,51	40,52	6,10	4,7
	$H_{(6b)}—C_{(4)}—C_{(5)}—H_{(5)}$	-80,90	0,98	-76,01	1,16	—

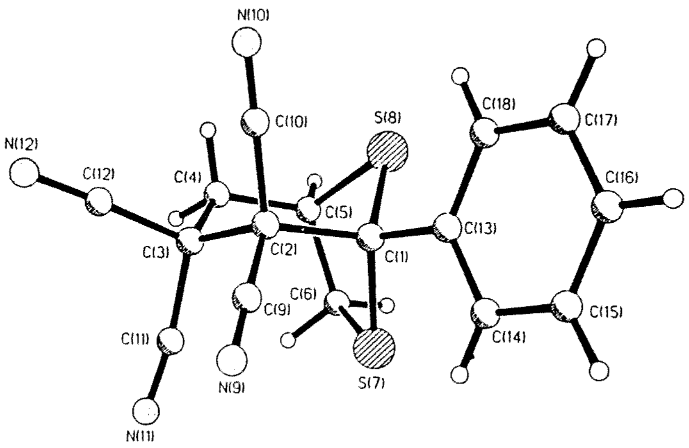


Fig. 1. Structure of the molecule of 1-phenyl-2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octane (I).

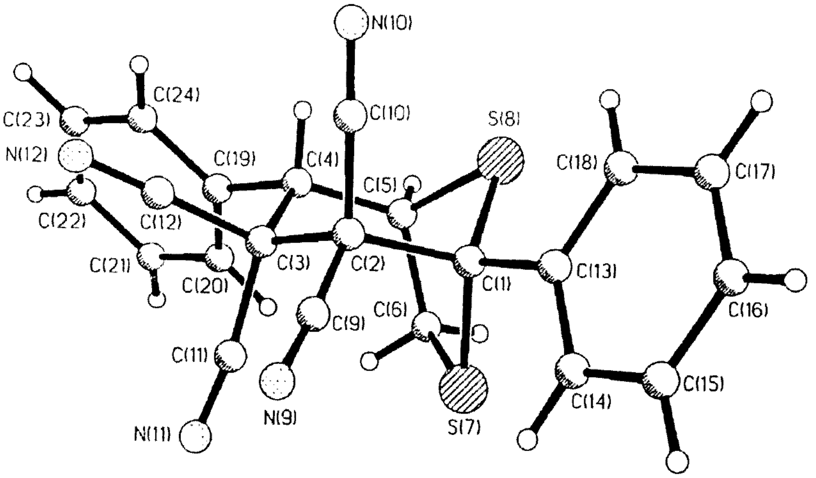


Fig. 2. Structure of the molecule of 1-*endo*-4-diphenyl-2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octane (II).

TABLE 4. Chemical Shifts (δ, ppm) in PMR Spectra of Compounds I-III

Compound	$H_{(4a)}$	$H_{(4b)}$	$H_{(5)}$	$H_{(6a)}$	$H_{(6b)}$	$1\text{-}R^1$	4-Ph
I	3,03	3,80	4,98	3,98	4,00	7,65...7,77	—
II	4,62	—	5,12	4,18	4,66	7,61...7,83	7,69...7,85
III	6,22	—	5,37	3,59	3,75	7,50...7,60*	7,70...7,85

---

*Aromatic protons from benzyl group; its CH_2 protons form an AB system, δ 3.92 and 3.98 ppm. ^2J = 14.3 Hz.

TABLE 5. Chemical Shifts (δ, ppm) in ^{13}C NMR Spectra of Compounds I-III

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	CN	C_{Ph}
I	74,05	55,05	41,97	38,48	48,70	44,88	111,51 112,35 113,69 113,73	129,74 130,03 131,65 135,10
II	74,15	57,14	48,63	52,35	53,22	42,91	111,43 111,96 112,23 113,14	129,87 130,82 130,05 131,86 130,18 134,71 130,24 134,98
III*	73,65	56,40	48,48	52,63	52,91	42,70	111,28 111,77 112,21 113,22	128,92 130,71 128,92 131,80 129,97 133,35 130,09 135,03

---

*$\delta_{(CH)_2}$ of benzyl group is 40.97 ppm.

TABLE 6. Crystallographic Data for Compounds I-III

	I	II	III
Empirical formula	$C_{16}H_{10}N_4S_2$	$C_{22}H_{14}N_4S_2$	$C_{23}H_{16}N_4S_2$
Mw	322,4	398,5	412,5
Space group	$P2_1/n$	$Pna2$	$P\bar{1}$
a (Å)	8,628(3)	19,631(6)	8,686(3)
b (Å)	8,143(2)	12,206(5)	11,112(4)
c (Å)	21,408(6)	8,023(2)	12,082(5)
α (°)	90	90	68,13(3)
β (°)	90,83(3)	90	72,83(3)
γ (°)	90	90	75,98(3)
V (Å^3)	1503(1)	1922(1)	1022,4(7)
Z	4	4	2
d_{calc} (g/cm^3)	1,424	1,377	1,340
Diffractometer	Siemens P3/PC	Siemens P3/PC	Syntex $P2_1$
$2\theta_{max}$	55°	55°	50°
Number of reflections	2665	2504	2871
R	0,048	0,062	0,032
R_w	0,049	0,059	0,033

The remaining geometric parameters have the usual values, and molecules I-III in the crystals are only joined by van der Waals interactions.

Since the substituents at the $C_{(6)}$ and $C_{(4)}$ carbon atoms can occupy *endo* and *exo* positions, it becomes necessary to look for a reliable method of determining their configuration other than by an x-ray structural study.*

---

*For convenience, *exo*-protons will subsequently be designated as $H_{(4a)}$ and $H_{(6a)}$ and *endo*-protons will be designated as $H_{(4b)}$ and $H_{(6b)}$.

TABLE 7. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors U ($Å^2 \times 10^3$) of Nonhydrogen Atoms in the Structure of I

Atom	x	y	z	U	Atom	x	y	z	U
$S_{(7)}$	4261(1)	1784(1)	7167(1)	40(1)	$C_{(6)}$	3952(4)	-413(3)	7028(1)	49(1)
$S_{(8)}$	5926(1)	369(1)	6119(1)	40(1)	$C_{(9)}$	2935(2)	4307(2)	6141(1)	31(1)
$N_{(9)}$	2410(2)	5505(2)	6306(1)	51(1)	$C_{(10)}$	4191(3)	2905(2)	5299(1)	32(1)
$N_{(10)}$	4633(3)	3042(3)	4805(1)	48(1)	$C_{(11)}$	4191(3)	1564(3)	6472(1)	37(1)
$N_{(11)}$	246(3)	1621(3)	6834(1)	55(1)	$C_{(12)}$	1231(3)	1692(3)	5377(1)	38(1)
$N_{(12)}$	426(3)	1923(3)	4963(1)	59(1)	$C_{(13)}$	6211(2)	3635(2)	6418(1)	32(1)
$C_{(1)}$	5042(2)	2245(2)	6398(1)	30(1)	$C_{(14)}$	6153(3)	4849(3)	6877(1)	42(1)
$C_{(2)}$	3611(2)	2718(2)	5944(1)	28(1)	$C_{(15)}$	7209(3)	6121(3)	6882(1)	51(1)
$C_{(3)}$	2252(2)	1377(2)	5932(1)	31(1)	$C_{(16)}$	8331(3)	6226(3)	6434(1)	51(1)
$C_{(4)}$	2870(3)	-416(3)	5896(1)	39(1)	$C_{(17)}$	8416(3)	5033(3)	5978(1)	45(1)
$C_{(5)}$	4221(3)	-790(3)	6345(1)	41(1)	$C_{(18)}$	7366(3)	3749(3)	5970(1)	38(1)

TABLE 8. Coordinates ($\times 10^3$) and Equivalent Isotropic Temperature Factors U ($Å^2 \times 10^2$) of Hydrogen Atoms in the Structure of I

Atom	x	y	z	U	Atom	x	y	z	U
$H_{(4a)}$	323(3)	-63(3)	547(1)	5(1)	$H_{(14)}$	538(3)	481(3)	717(1)	4(1)
$H_{(4b)}$	196(3)	-114(3)	598(1)	5(1)	$H_{(15)}$	718(3)	697(3)	720(1)	6(1)
$H_{(5)}$	452(3)	-192(3)	629(1)	5(1)	$H_{(16)}$	911(3)	710(3)	645(1)	5(1)
$H_{(6a)}$	471(3)	-100(3)	729(1)	5(1)	$H_{(17)}$	926(3)	508(3)	567(1)	4(1)
$H_{(6b)}$	283(3)	-66(3)	714(1)	5(1)	$H_{(18)}$	744(3)	294(3)	564(1)	5(1)

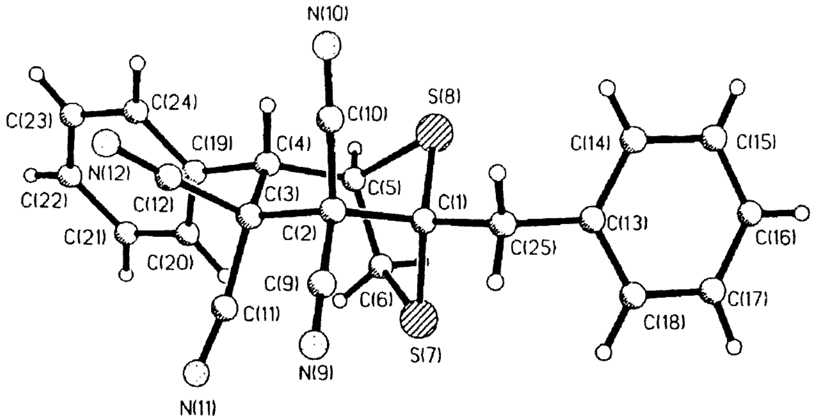


Fig. 3. Structure of the molecule of 1-benzyl-*endo*-4-phenyl-2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octane (III).

In our opinion, PMR spectroscopy combined with the modified Karplus equation [6] and calculations with the force field method (since compounds of the 7,8-dithiabicyclo[3.2.1]octane series contain up to 30 nonhydrogen atoms, optimization of the geometry by quantum chemical methods is problematic) is the most appropriate general method.

It is first necessary to demonstrate the applicability of the scheme of assignments in model compounds; for this purpose, we calculated the geometry of compounds I-III by the force field method (MMP2 program [7, 8]) and the vicinal SSCC for $H_{(4a)}$—$H_{(5)}$, $H_{(4b)}$—$H_{(5)}$, $H_{(6a)}$—$H_{(5)}$, and $H_{(6b)}$—$H_{(5)}$ protons were also calculated using the torsional angles obtained by both methods of calculation and with x-ray structural studies (Table 3). As Table 3 shows, the calculation satisfactorily reproduces the geometry of the compounds of this series; in isolated cases, the deviations from the experimental values can be corrected by optimization of the corresponding parameters.

TABLE 9. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors U ($Å^2 \times 10^3$) of Nonhydrogen Atoms in the Structure of II

Atom	x	y	z	U	Atom	x	y	z	U
$S_{(7)}$	2236(1)	6459(1)	1545	34(1)	$C_{(11)}$	3287(2)	5989(3)	4171(5)	30(1)
$S_{(8)}$	1953(1)	4130(1)	1117(2)	34(1)	$C_{(12)}$	3133(2)	4435(3)	5855(5)	26(1)
$N_{(9)}$	1889(2)	6563(3)	6461(7)	56(1)	$C_{(13)}$	1036(2)	5542(3)	2672(5)	33(1)
$N_{(10)}$	1593(2)	3194(3)	5310(6)	48(1)	$C_{(14)}$	817(2)	6589(3)	3079(7)	44(1)
$N_{(11)}$	3612(2)	6744(3)	4261(6)	48(1)	$C_{(15)}$	128(2)	6809(4)	3284(8)	56(2)
$N_{(12)}$	3278(2)	4105(3)	7133(5)	44(1)	$C_{(16)}$	-344(2)	5987(5)	3101(8)	57(2)
$C_{(1)}$	1795(2)	5297(3)	2463(5)	26(1)	$C_{(17)}$	-138(2)	4958(5)	2669(8)	58(2)
$C_{(2)}$	2121(2)	5028(3)	4258(5)	24(1)	$C_{(18)}$	555(2)	4708(4)	2457(7)	44(1)
$C_{(3)}$	2931(2)	4897(3)	4216(5)	21(1)	$C_{(19)}$	3945(2)	3974(3)	2804(5)	28(1)
$C_{(4)}$	3176(2)	4119(3)	2780(5)	23(1)	$C_{(20)}$	4390(2)	4583(4)	1834(8)	57(2)
$C_{(5)}$	2860(2)	4451(3)	1101(5)	29(1)	$C_{(21)}$	5087(2)	4401(5)	1897(9)	72(2)
$C_{(6)}$	2900(2)	5649(3)	545(6)	37(1)	$C_{(22)}$	5353(2)	3618(4)	2905(8)	55(2)
$C_{(9)}$	1967(2)	5900(3)	5482(6)	33(1)	$C_{(23)}$	4920(2)	2986(4)	3862(7)	47(1)
$C_{(10)}$	1817(2)	3990(3)	4864(6)	29(1)	$C_{(24)}$	4225(2)	3169(3)	3801(6)	36(1)

TABLE 10. Coordinates ($\times 10^3$) and Equivalent Isotropic Temperature Factors U ($Å^2 \times 10^2$) of Hydrogen Atoms in the Structure of II

Atom	x	y	z	U	Atom	x	y	z	U
$H_{(4)}$	299	341	303	5(1)	$H_{(17)}$	-47	440	250	6(1)
$H_{(5)}$	307	401	25	5(1)	$H_{(18)}$	70	398	217	5(1)
$H_{(6a)}$	285	569	-64	6(1)	$H_{(20)}$	421	516	115	5(1)
$H_{(6b)}$	334	594	84	6(1)	$H_{(21)}$	538	481	117	5(1)
$H_{(14)}$	115	716	322	7(1)	$H_{(22)}$	584	352	296	5(1)
$H_{(15)}$	-2	754	353	6(1)	$H_{(23)}$	510	242	457	5(1)
$H_{(16)}$	-82	613	330	6(1)	$H_{(24)}$	392	273	446	5(1)

At first glance, it is sufficient to compare the calculated heats of formation of two isomers for predicting the configuration of the compounds, but this only holds for the hypothesis of thermodynamic control.

Having the results of calculating the geometry and SSCC, it is possible to assign the signals in the PMR spectrum of compound I (Table 4). After separation of the signals of aromatic protons and the multiplet corresponding to the $H_{(5)}$ proton, two pairs of signals with geminal SSCC (^2J) of 16 and 11 Hz, respectively, remain. As Table 4 shows, the protons in the $C_{(4)}$ atom should have close vicinal SSCC (^3J) on the $H_{(5)}$ proton. On this basis, the pair of signals with $^2J = 16$ Hz and $^3J = 4.0$ and 2.9 Hz was respectively assigned to protons in the $C_{(4)}$ atom and confirmed by the absence of a 16 Hz SSCC in the PMR spectra of compounds II and III, where the $H_{(4b)}$ proton is substituted by phenyl. Another pair of signals was assigned to protons in the $C_{(6)}$ atom and the signal at 3.98 with$^3J = 5.6$ Hz was unambiguously assigned to the $H_{(6a)}$ *exo*-proton, while the one at 4.00 ppm with zero ^3J was assigned to the $H_{(6b)}$ *endo*-proton. The signals of the protons in the $C_{(6)}$ atom and in the PMR spectra of compounds II and III were assigned similarly.

Since the protons in the $C_{(4)}$ atom have similar vicinal SSCC on the $H_{(5)}$ proton, they are difficult to assign reliably even using the x-ray structural geometry. However, a "long-range" SSCC of $^5J = 0.9$ Hz, the so-called W constant [9], between the $H_{(6a)}$ proton and one of the protons in the $C_{(4)}$ atom is observed in the PMR spectra of compounds I-III. As Figs. 1-3 show, this constant can only be observed for two *exo*-protons and consequently, the signal at 3.30 with $^5J = 0.9$ Hz in the PMR spectrum of compound I is assigned to the $H_{(4a)}$ *exo*-proton, while the signal at 3.80 ppm with zero ^5J is assigned to the $H_{(4b)}$ *endo*-proton.

It is evident that the configuration of the position of protons in $C_{(4)}$ and $C_{(6)}$ atoms in the 7,8-dithiabicyclo[3.2.1]octane series and consequently the configuration of the corresponding substituents can be unambiguously established with the scheme of calculations and arguments laid out above.

TABLE 11. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors U (Å^2 $\times$ 10^3) of Nonhydrogen Atoms in the Structure of III

Atom	x	y	z	U	Atom	x	y	z	U
$S_{(7)}$	-4430(1)	-1325(1)	-6252(1)	44(1)	$C_{(12)}$	-1747(2)	2235(2)	-8421(2)	42(1)
$S_{(8)}$	-1934(1)	-1703(1)	-8363(1)	44(1)	$C_{(13)}$	-1546(2)	-3938(2)	-5890(2)	42(1)
$N_{(9)}$	-1907(2)	179(2)	-5065(2)	53(1)	$C_{(14)}$	-522(3)	-4621(2)	-6631(2)	61(1)
$N_{(10)}$	1361(2)	-167(2)	-8342(2)	55(1)	$C_{(15)}$	-750(5)	-5871(3)	-6477(3)	86(2)
$N_{(11)}$	-5416(2)	2101(2)	-6701(2)	58(1)	$C_{(16)}$	-1988(5)	-6427(3)	-5588(4)	91(2)
$N_{(12)}$	-959(2)	3038(2)	-8803(2)	67(1)	$C_{(17)}$	-2999(4)	-5768(3)	-4847(3)	82(2)
$C_{(1)}$	-2258(2)	-1461(2)	-6912(2)	35(1)	$C_{(18)}$	-2781(3)	-4528(2)	-4993(2)	58(1)
$C_{(2)}$	-1691(2)	-113(2)	-7157(2)	33(1)	$C_{(19)}$	-4027(2)	2142(2)	-9798(2)	39(1)
$C_{(3)}$	-2719(2)	1147(2)	-7948(2)	33(1)	$C_{(20)}$	-5708(3)	2391(2)	-9541(2)	52(1)
$C_{(4)}$	-3027(2)	936(2)	-9076(2)	35(1)	$C_{(21)}$	-6522(3)	3494(2)	-10271(3)	64(1)
$C_{(5)}$	-3592(2)	-383(2)	-8748(2)	41(1)	$C_{(22)}$	-5675(4)	4356(3)	-11254(3)	74(1)
$C_{(6)}$	-5053(3)	-754(2)	-7695(2)	51(1)	$C_{(23)}$	-4021(4)	4133(3)	-11508(3)	86(1)
$C_{(9)}$	-1806(2)	60(2)	-5974(2)	37(1)	$C_{(24)}$	-3198(3)	3021(2)	-10799(2)	64(1)
$C_{(10)}$	41(2)	-153(2)	-7824(2)	38(1)	$C_{(25)}$	-1306(3)	-2584(2)	-6039(2)	43(1)
$C_{(11)}$	-4262(2)	1603(2)	-7184(2)	39(1)					

TABLE 12. Coordinates ($\times 10^3$) and Equivalent Isotropic Temperature Factors U (Å^2 $\times$ 10^2) of Hydrogen Atoms in the Structure of III

Atom	x	y	z	U	Atom	x	y	z	U
$H_{(4)}$	-195(2)	87(2)	-959(1)	3(1)	$H_{(18)}$	-349(3)	-404(2)	-447(2)	7(1)
$H_{(5)}$	-375(2)	-40(2)	-948(2)	5(1)	$H_{(20)}$	-629(2)	181(2)	-884(2)	6(1)
$H_{(6a)}$	-544(3)	-144(2)	-779(2)	7(1)	$H_{(21)}$	-765(3)	361(2)	-1003(2)	9(1)
$H_{(6b)}$	-595(3)	-4(2)	-768(2)	6(1)	$H_{(22)}$	-621(3)	510(2)	-1177(2)	9(1)
$H_{(14)}$	36(3)	-423(2)	-717(2)	7(1)	$H_{(23)}$	-340(3)	466(3)	-1215(2)	11(1)
$H_{(15)}$	-6(3)	-627(3)	-695(2)	10(1)	$H_{(24)}$	-199(3)	288(2)	-1100(2)	7(1)
$H_{(16)}$	-211(4)	-728(3)	-544(3)	13(1)	$H_{(25a)}$	-17(2)	-251(2)	-635(2)	5(1)
$H_{(17)}$	-393(3)	-609(3)	-421(3)	11(1)	$H_{(25b)}$	-166(2)	-241(2)	-525(2)	4(1)

An interesting finding which has not yet been logically explained merits mention. The signal of the $H_{(4a)}$ proton in the PMR spectrum of compound III is anomalously shifted to weak fields by 1.6 (6.22 instead of 4.62 ppm for compound II). As the figures and tables show, the geometry of the central ring changes insignificantly, and the benzyl substituent is too far away to cause such a sharp change in the chemical shift.

The signals of quaternary $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ in the ^{13}C NMR spectra of compounds I-III (Table 5) were assigned with consideration of the effect of the substituents and long-range C—H SSCC. For example, in substitution of the $H_{(4b)}$ proton by phenyl in going from compound I to compound II, the following shifts of the signals $\Delta\delta$ to weak fields are observed: 13.87 for $C_{(4)}$, 6.66 for $C_{(3)}$, and 2.69 ppm for $C_{(2)}$. Incorporation of phenyl affects the chemical shift of the $C_{(2)}$ atom to a much smaller degree than for $C_{(3)}$, and for this reason the assignment of these signals to the corresponding atoms raises no doubt. In addition, the C—$H_{(4)}$ long-range SSCC are equal to 6.5 and 3.6 Hz for $C_{(2)}$ atoms of compounds I and II and 9.5, 5.1, and 7.5 Hz for $C_{(3)}$. The triplets of the $C_{(4)}$ (J 140.2 Hz) and $C_{(6)}$ atoms (J 147.7 Hz) in the spectrum of compound I were assigned with selective decoupling from $H_{(4)}$ and $H_{(6)}$ protons, respectively, and the doublets of $C_{(4)}$ (J 136.6 Hz) and $C_{(5)}$ atoms (J 145.7 Hz) in the spectrum of compound II were assigned by decoupling from $H_{(4)}$ and $H_{(5)}$ protons. A negative γ shift of -1.97 and -2.18 ppm, respectively, for the $C_{(6)}$ atom is observed in compounds II and III, and they are close to the increment of phenyl in the γ position of $\Delta\delta\gamma = -2.6$ ppm reported in [9]. Substitution of the phenyl at the $C_{(1)}$ atom by benzyl in going from compounds I and II to compound III virtually does not alter the chemical shift of this atom. If we compare the increments of the phenyl ($\Delta\delta\alpha = 22.1$) and benzyl calculated with the equation

$$\Delta\delta\alpha\text{-Bn} = \Delta\delta\beta\text{-Ph} + \Delta\delta\alpha\text{-Me} = 9{,}1 + 9{,}3 = 18{,}4 \text{ ppm.},$$

this observation can easily be explained.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 577 in KCl pellets. The ^1H and ^{13}C NMR spectra were recorded on a VXR-Varian-400 spectrometer in DMF-D_7 with TMS as the internal standard.

The data from elemental analysis for C, H, N, and S corresponded to the calculations.

Synthesis of 7,8-dithiabicyclo[3.2.1]octanes (I and II) was described previously in [1].

1-Benzyl-*endo*-4-phenyl-2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octane (III). A solution of 1.71 g (6 mmole) of dithiophenylacetic acid cinnamyl ester and 0.77 g (6 mmole) of tetracyanoethylene in 5 m of absolute acetonitrile was boiled under argon for 3 h, cooled, and the precipitated sediment of compound III was filtered off and crystallized from acetonitrile. Yield of 2.05 g (83%). Mp = 221-222°C (with decomposition).

X-ray Structural Studies

The crystal structure data for compounds I-III are reported in Table 6. The cell parameters and reflection intensities for compounds I-III were measured at room temperature using λMoKα radiation (graphite monochromator, $\lambda = 0.71073$). All structures were interpreted by a direct method and refined by total-matrix *MNC* in the anisotropic approximation for all nonhydrogen atoms. The objectively determined H atoms were more precisely defined isotropically in structures I and III and were considered in structure II using the "rider" model. Weighted schemes $w^{-1} = \sigma^2(F) + k(F)$ were used in the refinement, where $k = 0.0001$, 0.0003, and 0.0001 for compounds I, II, and III, respectively. Refinement of the inverted structure of II resulted in close values of the *R* factors, which did not allow establishing the absolute structure of compound II. All calculations were performed with the SHELXTL PLUS software package [10]. The coordinates of the atoms are reported in Tables 7-12, and the bond lengths and valence angles are given in Tables 1 and 2.

The research was financially supported by the Russian Fund for Fundamental Research, project code 93-03-04290, the International Science Foundation, grant M5Y000, and the State Committee of the Russian Federation on VO (TPS "Fine Organic Synthesis"), Project No. FT-12.

REFERENCES

1. I. V. Magedov, V. N. Drozd, S. Yu. Shapakin, D. S. Yufit, and Yu. T. Struchkov, Sulfur Lett., **17** (1994).
2. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc. Perkin II, No. 1, 1 (1987).
3. H. Gotthardt, O. M. Huss, and S. Schog-Tribbensee, Chem. Ber., **114**, 285 (1981).
4. B. Kojic-Prodic, Z. Ruzic-Toros, and J. J. Herak, Acta Crystallogr., **B37**, 214 (1981).
5. I. R. Fjeldskaar, D. Grace, C. Romming, and L. Scattebol, Acta Chem. Scand., **B42**, 280 (1988).
6. C. A. G. Haasnoot, F. A. A. M. de Leeuw, and C. Altona, Tetrahedron, **36**, 2783 (1980).
7. N. L. Allinger and J. T. Sprague, J. Am. Chem. Soc., **95**, 3893 (1973).
8. J. Kao and N. L. Allinger, J. Am. Chem. Soc., **99**, 975 (1977).
9. H. Günther, Introduction to NMR Spectroscopy [Russian translation], Mir, Moscow (1984), pp. 132, 404.
10. G. M. Sheldrick, SHELXTL PLUS. PC Version, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin (1989).