

# Dichotomy in the reaction between cinnamyl dithiocarboxylates and tetracyanoethylene with the formation of 7,8-dithiabicyclo[3.2.1]octanes and dithioacyloxycyclopentanes\*

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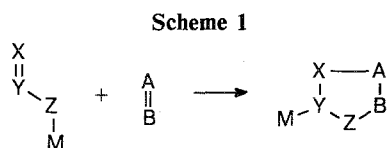
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The reaction of cinnamyl dithiocarboxylates (**1**) containing electron-donating substituents at the central carbon atom of the dithioester group ( $R = p\text{-MeOC}_6\text{H}_4$ ,  $\text{EtO}$ , and  $p\text{-Tol}$ ) with tetracyanoethylene affords 2,2,3,3-tetracyano-4-*endo*-phenyl-7,8-dithiabicyclo[3.2.1]octanes (**2**) as well as isomeric 3,3,4,4-tetracyano-2-phenyl-*trans*-1-dithioacyloxycyclopentanes (**3**). Dithiabicyclooctanes **2** rearrange to the corresponding cyclopentanes **3** upon thermolysis.

**Key words:** cinnamyl dithiocarboxylates; tetracyanoethylene; 2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octanes; 3,3,4,4-tetracyano-1-dithioacyloxycyclopentanes.

Examples of cycloaddition reactions accompanied by a sigmatropic shift are scarce in the literature. These reactions may be presented in general form as follows (Scheme 1).



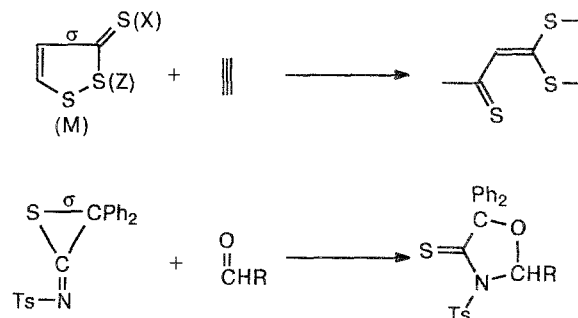
This scheme describes the reaction only formally and does not deal with mechanisms of interactions, which may be highly diversified.

Particular examples of reactions of this type in which the M migrant is bonded to the Y atom by a  $\sigma$  bond are known (Scheme 2).<sup>1,2</sup>

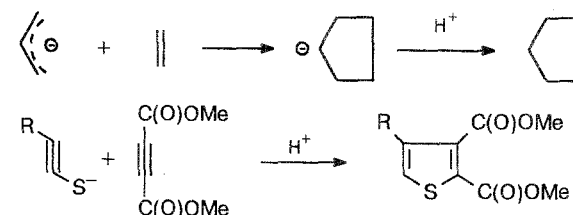
Reactions of ionic cycloaddition, for example, anionic [3+2] cycloaddition (Scheme 3)<sup>3,4</sup> as well as reactions of  $\eta^1$ -allyl and propargyl derivatives of transition metals with tetracyanoethylene (Scheme 4),<sup>5</sup> may also be considered as a special case of these conversions.

Reactions of allyl(propargyl)silanes with electron-deficient multiple bonds, which result in formation of five-membered cycles with concurrent 1,2-migration of the trialkylsilyl group (the Danheiser reaction, Scheme 5), have been studied intensively in recent years.

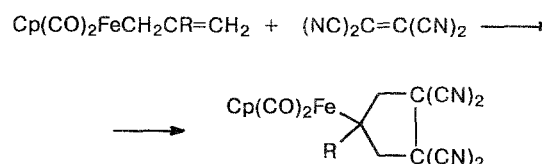
**Scheme 2**



**Scheme 3**



**Scheme 4**



\* Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).

† Deceased in August, 1995.

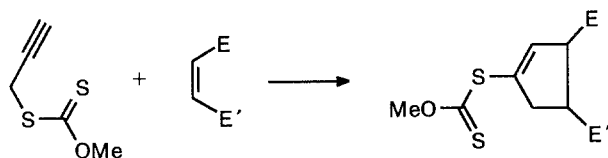
Scheme 5



This method is suitable for synthesis of cyclopentanes and cyclopentenones,<sup>6</sup> dihydrofurans and pyrrolines,<sup>7</sup> isoxazoles,<sup>8</sup> azulenes,<sup>9</sup> and furans.<sup>10</sup>

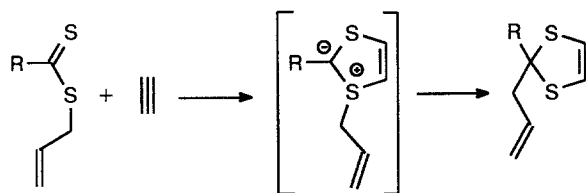
The reaction of *O*-methyl *S*-propargyl xanthate with derivatives of fumaric and maleic acids affords substituted *O*-methyl *S*-1-cyclopentyl xanthates upon heating (Scheme 6).<sup>11</sup>

Scheme 6



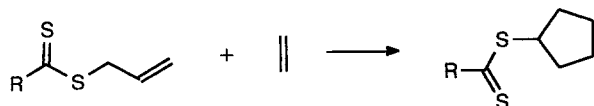
We have found<sup>12</sup> that the system of connected allyl and 1,3-dithiaallyl groups, which form the structure of allyl ethers of dithiocarboxylic acids, is able not only to be subjected to [1,3] and [3,3] sigmatropic rearrangements but to react with activated triple bonds as well. 2,2-Disubstituted 1,3-dithiols are the reaction products. The reaction mechanism involves [3+2] cycloaddition of the 1,3-dithiaallyl fragment at the triple bond followed by a [1,2] and [2,3] sigmatropic shift of the allyl group in the intermediate betaine (Scheme 7).

Scheme 7



However, in principle an alternative mechanism may be realized: formal [3+2] cycloaddition of the allyl fragment at the activated unsaturated bond followed by [1,2] or [2,3] migration of the dithiocarboxylic group (Scheme 8).

Scheme 8



Previously, we have found<sup>13</sup> an unusual reaction of allyl ethers of dithiocarboxylic acids with tetracyanoethylene on boiling in acetonitrile, which affords 1-*R*-2,2,3,3-tetracyano-7,8-dithiabicyclo[3.2.1]octanes (**2**). Continuing these studies, we found that cinnamyl dithiocarboxylates containing electron-donating substituents at the central C atom of the dithioester group (**1a–c**) react with tetracyanoethylene (TCNE) to form not only the corresponding 7,8-dithiabicyclo[3.2.1]octanes (**2a–c**) but the products of [3+2] cycloaddition, which is followed by a 1,2-shift of the dithioacyloxy group, namely, 3,3,4,4-tetracyano-2-phenyl-*trans*-1-dithioacyloxy-cyclopentanes (**3a–c**) as well (Scheme 9).

Cinnamyl ethers **1a,b** containing strong  $\pi$  or  $n$  donors at the mentioned position react with TCNE in acetonitrile at 20 °C to form exclusively bicyclooctanes **2a,b**. When the reaction is performed at 80 °C, cyclopentanes **3a,b** are formed; when a weaker  $\pi$  donor (*p*-Tol, dithioester **1c**) is present, a mixture of isomeric cyclopentane **3c** and bicyclooctane **2c** is formed in the ratio ~1 : 1 (according to the <sup>1</sup>H NMR spectra).

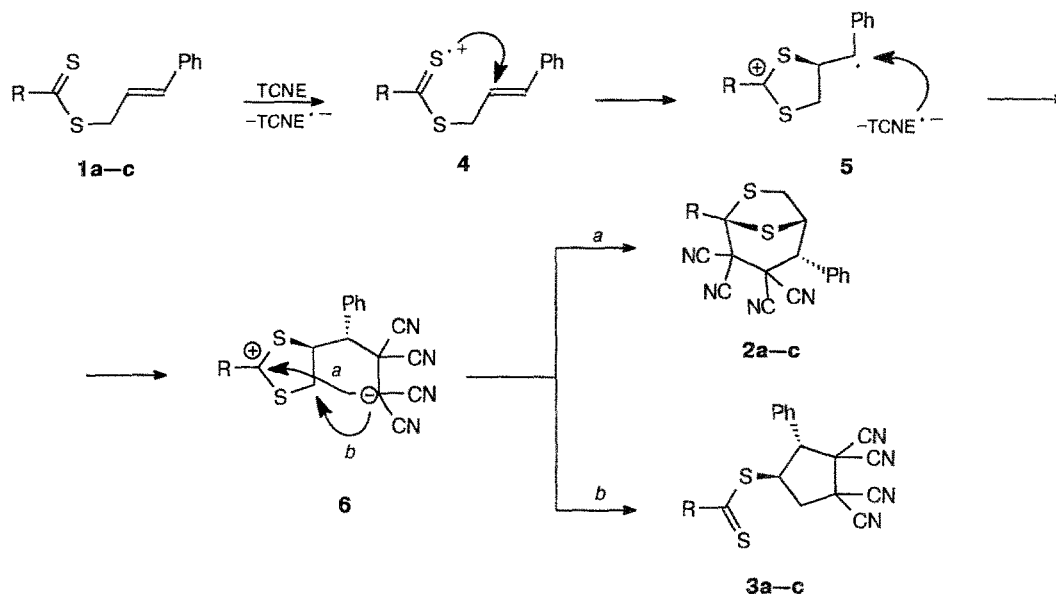
We proposed the following mechanism of formation of isomeric adducts **2** and **3**, which involves formation of common intermediates **4**, **5**, and **6** in the initial stages: (1) single-electron transfer between cinnamyl dithiocarboxylates and tetracyanoethylene with the formation of radical cation **4** and radical anion TCNE; (2) cyclization of radical cation **4** to isomeric cyclic radical anion **5**; (3) addition of radical anion TCNE to cyclic radical cation **5**. Spatial arrangement of the Ph substituent in isomeric adducts (*trans*- in cyclopentanes **3** and *endo*- in bicyclooctanes **2**) is reasonably attributable to a synchronous or successive *anti* attack at the S atom of the dithioester group of radical cation **4** and radical anion TCNE at the *trans* double bond of the cinnamyl fragment. Dichotomy of the reaction is determined by the possibility of stabilization of intermediate zwitterion **6** in two ways (see Scheme 9): *a*, attack of the carbanion center at the central C atom of the former dithioester group with the formation of 7,8-dithiabicyclo[3.2.1]octanes **2**; *b*, intramolecular nucleophilic substitution with regeneration of the dithiocarboxylate group resulting in cyclopentanes **3**.

If it is assumed that the stage of cycloaddition of betaine **6** to 7,8-dithiabicyclo[3.2.1]octanes **2** is reversible, it is expected that it will be possible to choose conditions of a rearrangement of compounds **2** to thermodynamically more stable cyclopentanes **3**.

Actually, on thermolysis (170–210 °C) of bicyclooctanes **2a–e** bearing  $\pi$  donor substituents at position 1, these bicyclooctanes readily rearrange to cyclopentanes **3a–e** in high yields (Scheme 10). Note that some cyclopentanes (**3d,e**), which are not formed in detectable amounts on direct reaction of the corresponding cinnamyl dithiocarboxylates **1d,e** with TCNE in boiling acetonitrile, were prepared by this procedure.

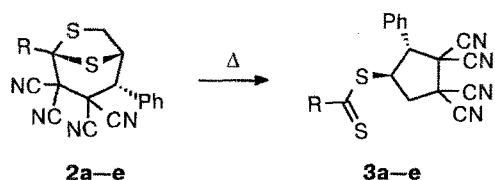
An alternative mechanism of the rearrangement with complete dissociation into the initial cinnamyl dithiocar-

Scheme 9



R = *p*-MeOC<sub>6</sub>H<sub>4</sub> (**a**), EtO (**b**), *p*-MeC<sub>6</sub>H<sub>4</sub> (**c**)

Scheme 10



R = *p*-MeOC<sub>6</sub>H<sub>4</sub> (**a**), EtO (**b**), *p*-MeC<sub>6</sub>H<sub>4</sub> (**c**),  
Ph (**d**), *p*-ClC<sub>6</sub>H<sub>4</sub> (**e**)

boxylates and TCNE should be rejected because when thermolysis of bicyclooctane **2a** proceeds in the presence of *S*-cinnamyl *O*-ethyl xanthate **1b**, only the product of an intermolecular rearrangement, cyclopentane **3a**, was detected in the reaction mixture, while cyclopentane **3b**, formation of which would be expected with the dissociation mechanism, is completely absent (monitoring by <sup>1</sup>H NMR).

The structure of molecule **3a** (Fig. 1) was unambiguously established by X-ray structural analysis. The five-membered cycle adopts a distorted half-chair conforma-

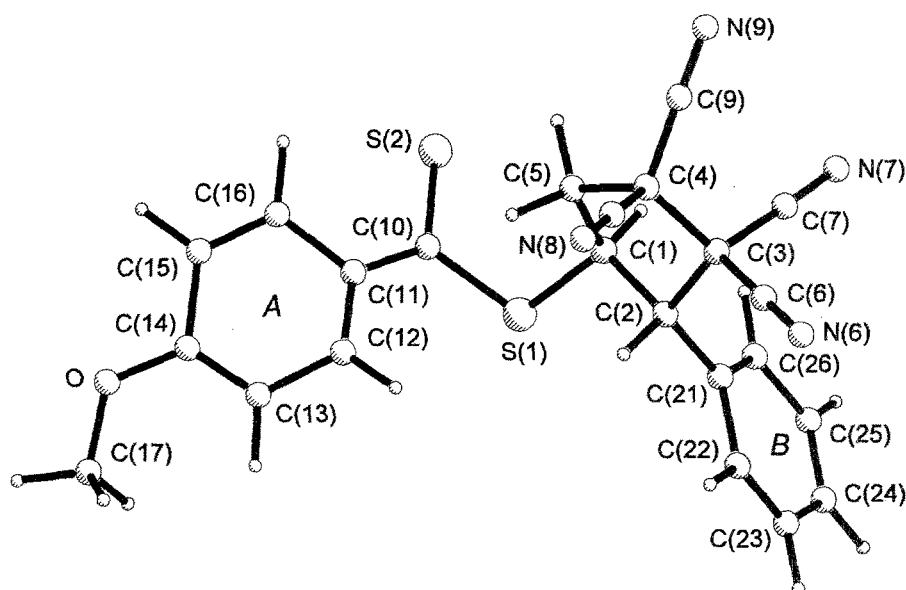


Fig. 1. Structure of molecule **3a**.

tion; the C(3) and C(4) atoms deviate from the C(5)C(1)C(2) plane by 0.39 and  $-0.28$  Å, respectively. The methoxyphenyldithiocarboxylate and phenyl (*B*) substituents are in *trans* positions with respect to the five-membered cycle; the C(2)—C(21) and C(1)—S(1) bonds are in a pseudoequatorial orientation.

The dithiocarboxylate group is slightly rotated with respect to the plane of the benzene ring *A* (the S(1)—C(10)—C(11)—C(12) torsion angle is  $-18.8^\circ$ ), while the methoxy group is virtually coplanar with the phenyl ring.

The C—C bond lengths in the five-membered cycle, as usual, correlate with the number of substituents at the corresponding atoms; the C(2)—C(3) and C(3)—C(4) bonds are the most elongated (both bond, to  $1.574(5)$  Å), which can be caused also by the electron density shift from these bonds to the C(sp<sup>3</sup>)—CN bonds with electron-withdrawing cyano groups. The remaining bond lengths in the molecule are close to normal values.

### Experimental

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a VXR-Varian-400 instrument (400 MHz). Mass spectra were recorded on a Varian MAT 311A spectrometer.

**Table 1.** Atomic coordinates of nonhydrogen atoms ( $\times 10^4$ ) in molecule **3a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	7967(1)	4191(1)	1536(1)
S(2)	6138(1)	452(5)	2845(1)
O	5055(3)	7581(2)	−852(2)
N(6)	11135(4)	1217(3)	2059(3)
N(7)	10158(3)	1940(2)	4968(3)
N(8)	7993(3)	1739(3)	388(3)
N(9)	7692(4)	528(3)	3377(3)
C(1)	8438(3)	3482(2)	2673(2)
C(2)	9708(3)	3132(2)	2601(2)
C(3)	9668(3)	2148(2)	2913(2)
C(4)	8299(3)	1900(2)	2447(2)
C(5)	7607(3)	2708(2)	2719(3)
C(6)	10520(4)	1621(3)	2451(3)
C(7)	9945(3)	2030(2)	4080(3)
C(8)	8109(3)	1791(2)	1281(3)
C(9)	7942(4)	1108(3)	2933(3)
C(10)	6743(3)	4764(2)	1832(3)
C(11)	6318(3)	5478(2)	1089(2)
C(12)	7035(3)	5829(3)	438(3)
C(13)	6643(3)	6528(3)	−222(3)
C(14)	5523(3)	6892(2)	−244(3)
C(15)	4793(3)	6547(3)	390(3)
C(16)	5181(3)	5850(3)	1036(3)
C(17)	5768(5)	7947(3)	−1531(4)
C(21)	10821(3)	3603(2)	3205(3)
C(22)	11863(4)	3585(3)	2801(3)
C(23)	12922(4)	3976(4)	3360(4)
C(24)	12933(4)	4395(3)	4292(4)
C(25)	11906(4)	4413(3)	4692(4)
C(26)	10852(4)	4019(3)	4160(3)

X-ray diffraction analysis was performed on a four-circle automated Siemens P3/PC diffractometer (Mo-K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073$  Å) at room temperature; all calculations were carried out on a PC computer using the SHELXTL PLUS program package. Orange crystals of **3a** (from benzene) are monoclinic,  $a = 11.260(5)$  Å,  $b = 15.436(7)$  Å,  $c = 12.891(4)$  Å,  $\beta = 102.57(2)^\circ$ ,  $V = 2186.8(1.6)$  Å<sup>3</sup> (using 16 reflections with  $25^\circ < 2\theta < 26^\circ$ ), space group  $P2_1/c$ ,  $Z = 4$ ,  $C_{23}H_{16}N_4OS_2$ ,  $M = 428.5$ ,  $d_{\text{calc}} = 1.30$  g cm<sup>−3</sup>,  $\lambda(\text{Mo-K}\alpha) = 2.7$  cm<sup>−1</sup>. Intensities of 6651 reflections were measured using a  $\theta/2\theta$  scanning technique, of which 6360 were independent (the discrepancy between equivalents was 0.038), with  $2\theta \leq 60^\circ$ ; 3050 reflections with  $I > 3\sigma(I)$  were used in calculations. The structure was solved by the direct method and refined by the full-matrix least-squares method to  $R = 0.069$ ,  $R_w = 0.067$ . All nonhydrogen atoms were refined anisotropically; all H atoms were included in the refinement using a riding model (271 refinable parameters). The following weighting scheme was used:  $w^{-1} = \delta^2(F) + 0.0003F^2$ ; the figure of merit was 2.23. Atomic coordinates in molecule **3a** are given in Tables 1 and 2; the principal bond lengths and bond angles are listed in Tables 3 and 4, respectively.

**3,3,4,4-Tetracyano-2-phenyl-trans-1-(dithioacyloxy)cyclopentanes (3).** **Method A.** A solution of cinnamyl dithiocarboxylate **1a-c** (3.4 mmol) and tetracyanoethylene (3.4 mmol) in acetonitrile (2 mL) was boiled for 3 h under an argon atmosphere, then the solution was cooled, and the solvent was

**Table 2.** Atomic coordinates of hydrogen atoms ( $\times 10^3$ ) in molecule **3a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	853	382	331
H(2)	974	315	186
H(5a)	685	28	221
H(5b)	743	265	341
H(12)	781	557	45
H(13)	715	676	−67
H(15)	401	680	38
H(16)	466	561	146
H(17a)	534	843	−191
H(17b)	653	814	−112
H(17c)	591	751	−203
H(22)	1185	329	214
H(23)	1365	396	309
H(24)	1366	468	467
H(25)	1191	471	535
H(26)	1014	402	445

**Table 3.** Principal bond lengths (*d*) in molecule **3a**

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
S(1)—C(1)	1.813(3)	C(1)—C(5)	1.527(5)
S(1)—C(10)	1.748(4)	C(2)—C(3)	1.574(5)
S(2)—C(10)	1.640(4)	C(2)—C(21)	1.510(4)
O—C(14)	1.359(4)	C(3)—C(4)	1.574(5)
O—C(17)	1.426(6)	C(3)—C(6)	1.479(5)
N(6)—C(6)	1.130(6)	C(3)—C(7)	1.479(5)
N(7)—C(7)	1.127(5)	C(4)—C(5)	1.550(5)
N(8)—C(8)	1.131(5)	C(4)—C(8)	1.481(5)
N(9)—C(9)	1.132(6)	C(4)—C(9)	1.469(6)
C(1)—C(2)	1.552(5)	C(10)—C(11)	1.471(5)

**Table 4.** Principal bond angles ( $\omega$ ) in molecule **3a**

Angle	$\omega/\text{deg}$	Angle	$\omega/\text{deg}$
C(1)—S(1)—C(10)	103.5(2)	C(3)—C(4)—C(9)	112.1(3)
C(14)—O—C(17)	117.8(3)	C(5)—C(4)—C(9)	112.0(3)
S(1)—C(1)—C(2)	105.8(2)	C(8)—C(4)—C(9)	110.2(3)
S(1)—C(1)—C(5)	115.4(2)	C(1)—C(5)—C(4)	106.2(3)
C(2)—C(1)—C(5)	108.0(3)	N(6)—C(6)—C(3)	177.1(3)
C(1)—C(2)—C(3)	104.0(3)	N(7)—C(7)—C(3)	180.0(5)
C(1)—C(2)—C(21)	118.2(3)	N(8)—C(8)—C(4)	177.3(4)
C(3)—C(2)—C(21)	113.5(2)	N(9)—C(9)—C(4)	175.0(4)
C(2)—C(3)—C(4)	102.6(2)	S(1)—C(10)—S(2)	122.9(2)
C(2)—C(3)—C(6)	111.7(3)	S(1)—C(10)—C(11)	113.4(3)
C(4)—C(3)—C(6)	112.3(3)	S(2)—C(10)—C(11)	123.7(3)
C(2)—C(3)—C(7)	111.6(3)	C(10)—C(11)—C(12)	122.3(3)
C(4)—C(3)—C(7)	109.3(3)	C(10)—C(11)—C(16)	120.4(3)
C(6)—C(3)—C(7)	109.2(3)	C(12)—C(11)—C(16)	117.2(3)
C(3)—C(4)—C(5)	102.5(2)	O—C(14)—C(13)	124.7(4)
C(3)—C(4)—C(8)	109.2(3)	O—C(14)—C(15)	115.9(3)
C(5)—C(4)—C(8)	110.6(3)	C(13)—C(14)—C(15)	119.4(3)

evaporated under reduced pressure. The product was crystallized from a 1 : 1 hexane—benzene mixture.

**3,3,4,4-Tetracyano-*trans*-1-(4-methoxydithiobenzoyloxy)-2-phenylcyclopentane (3a).** The yield was 1.8 mmol (53 %), m.p. 118–120 °C. Found (%): C, 64.30; H, 3.74; N, 13.10; S, 15.02.  $\text{C}_{23}\text{H}_{16}\text{N}_4\text{OS}_2$ . Calculated (%): C, 64.46; H, 3.76; N, 13.07; S, 14.96.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 3.01 (dd, 1 H, C(5)H(a)); 3.79 (dd, 1 H, C(5)H(b),  $J_{\text{H(a),H(b)}} = 15.5$  Hz); 3.86 (s, 3 H,  $\text{OCH}_3$ ); 4.28 (d, 1 H, C(2)H,  $J_{\text{C(2)H,C(1)H}} = 11.7$  Hz); 5.21 (m, 1 H, C(1)H,  $J_{\text{C(1)H,C(5)H(a)}} = 4.5$  Hz,  $J_{\text{C(1)H,C(5)H(b)}} = 10.7$  Hz); 6.85 (d, 2 H,  $\text{CH}_m$  arom.); 8.01 (d, 2 H,  $\text{CH}_o$  arom.,  $J_{\text{H}_o,\text{H}_m} = 8.8$  Hz); 7.52 (m, 5 H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 43.40 (C(5)); 43.43 (C(4)); 46.72 ( $\text{OCH}_3$ ); 51.31 (C(3)); 55.7 (C(2)); 56.45 (C(1)); 108.5 (CN); 109.47 (CN); 109.94 (CN); 110.85 (CN); 113.86 (CH arom.); 128.33 (C arom.); 128.47 (CH arom.); 129.5 (CH arom.); 129.89 (CH arom.); 131.12 (CH arom.); 136.28 (C arom.); 164.81 (C arom.); 220.97 (CS).

**3,3,4,4-Tetracyano-*trans*-1-(ethoxydithioformyloxy)-2-phenylcyclopentane (3b).** The yield was 1.6 mmol (48 %), m.p. 112–113 °C. Found (%): C, 59.11; H, 3.82; N, 15.16; S, 17.65.  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{OS}_2$ . Calculated (%): C, 58.99; H, 3.85; N, 15.29; S, 17.50.  $^1\text{H}$  NMR ( $\text{DMF-d}_7$ ),  $\delta$ : 1.49 (t, 3 H,  $\text{CH}_3$ ); 3.68 (dd, 1 H, C(5)H(a)); 4.05 (dd, 1 H, C(5)H(b),  $J_{\text{H(a),H(b)}} = 14.8$  Hz); 4.77 (m, 2 H,  $\text{CH}_2$ ,  $J_{\text{CH}_2,\text{CH}_3} = 7.1$  Hz); 4.99 (d, 1 H, C(2)H,  $J_{\text{C(2)H,C(1)H}} = 11.9$  Hz); 5.18 (m, 1 H, C(1)H,  $J_{\text{C(1)H,C(5)H(a)}} = 8.5$  Hz,  $J_{\text{C(1)H,C(5)H(b)}} = 8.4$  Hz); 7.75 (m, 5 H, Ph).

**3,3,4,4-Tetracyano-*trans*-1-(4-methyldithioformyloxy)-2-phenylcyclopentane (3c).** The yield was 1.7 mmol (50 %), m.p. 120–121 °C. Found (%): C, 66.85; H, 3.97; N, 13.66; S, 15.62.  $\text{C}_{23}\text{H}_{16}\text{N}_4\text{S}_2$ . Calculated (%): C, 66.96; H, 3.91; N, 13.58; S, 15.54.  $^1\text{H}$  NMR ( $\text{DMF-d}_7$ ),  $\delta$ : 2.40 (s, 3 H,  $\text{CH}_3$ ); 3.60 (dd, 1 H, C(5)H(a)); 3.94 (dd, 1 H, C(5)H(b),  $J_{\text{H(a),H(b)}} = 16.0$  Hz); 4.40 (d, 1 H, C(2)H,  $J_{\text{C(2)H,C(1)H}} = 12.1$  Hz); 5.22 (m, 1 H, C(1)H,  $J_{\text{C(1)H,C(5)H(a)}} = 4.5$  Hz,  $J_{\text{C(1)H,C(5)H(b)}} = 11.1$  Hz); 7.18 (d, 2 H,  $\text{CH}_m$  arom.); 7.96 (d, 2 H,  $\text{CH}_o$  arom.,  $J_{\text{H}_o,\text{H}_m} = 10.1$  Hz); 7.33 (m, 5 H, Ph).

**Method B.** 2,2,3,3-Tetracyano-4-*endo*-phenyl-7,8-dithiabicyclo[3.2.1]octanes **2a**, **2b**, **2d**, and **2e** (1.50 mmol) were heated under an argon atmosphere to 177 °C, 170 °C, 210 °C, and 220 °C, respectively. Crystallization from a 1 : 1 hexane—

benzene mixture affords compounds **3a** (1.47 mmol, 98 %), **3b** (1.48 mmol, 99 %), **3d**, and **3e**, respectively.

**3,3,4,4-Tetracyano-2-phenyl-*trans*-1-(dithiobenzoyloxy)-cyclopentane (3d).** The yield was 1.47 mmol (98 %), m.p. 122–123 °C. Found (%): C, 66.20; H, 3.57; N, 14.12; S, 16.00.  $\text{C}_{22}\text{H}_{14}\text{N}_4\text{OS}_2$ . Calculated (%): C, 66.31; H, 3.54; N, 14.06; S, 16.09.  $^1\text{H}$  NMR ( $\text{DMF-d}_7$ ),  $\delta$ : 3.54 (dd, 1 H, C(5)H(a)); 4.00 (dd, 1 H, C(5)H(b),  $J_{\text{H(a),H(b)}} = 14.8$  Hz); 5.24 (d, 1 H, C(2)H,  $J_{\text{C(2)H,C(1)H}} = 12.0$  Hz); 5.48 (m, 1 H, C(1)H,  $J_{\text{C(1)H,C(5)H(a)}} = 8.5$  Hz,  $J_{\text{C(1)H,C(5)H(b)}} = 8.4$  Hz); 7.85 (m, 10 H, 2 Ph).

***trans*-1-(4-Chlorodithiobenzoyloxy)-3,3,4,4-tetracyano-2-phenylcyclopentane (3e).** The yield was 1.44 mmol (96 %), m.p. 127–128 °C. Found (%): C, 60.83; H, 2.97; N, 12.80; S, 14.72.  $\text{C}_{22}\text{H}_{13}\text{ClN}_4\text{OS}_2$ . Calculated (%): C, 61.03; H, 3.03; N, 12.94; S, 14.81.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 3.03 (dd, 1 H, C(5)H(a)); 3.77 (dd, 1 H, C(5)H(b),  $J_{\text{H(a),H(b)}} = 15.5$  Hz); 4.28 (d, 1 H, C(2)H,  $J_{\text{C(2)H,C(1)H}} = 11.6$  Hz); 5.13 (m, 1 H, C(1)H,  $J_{\text{C(1)H,C(5)H(a)}} = 4.4$  Hz,  $J_{\text{C(1)H,C(5)H(b)}} = 10.1$  Hz); 7.36 (d, 2 H,  $\text{CH}_m$  arom.); 7.53 (d, 2 H,  $\text{CH}_o$  arom.,  $J_{\text{H}_o,\text{H}_m} = 7.5$  Hz); 7.89 (m, 5 H, Ph).

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