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The Reaction of Allylic Esters of Dithiocarboxylic Acids with Tetracyanoethylene Affording 3,3,4,4-Tetracyano-6,8-dithiabicyclo[3.2.1]octanes.

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Abstract: A range of substituted 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes, viz. compounds **5d-g**, **5j-m**, and **5o-u**, have been synthesized from the corresponding allyl dithiocarboxylates by a cation radical cycloaddition reaction, using tetracyanoethylene **2** in acetonitrile. The reaction scope has been studied and the mechanism proposed on the basis of the dithioester's chemical behaviour in respect to oxidizing agents, mass-spectrometry data, the substituent effect analysis as well as by quantum chemical calculations by the MINDO/3 method in UHF approach.

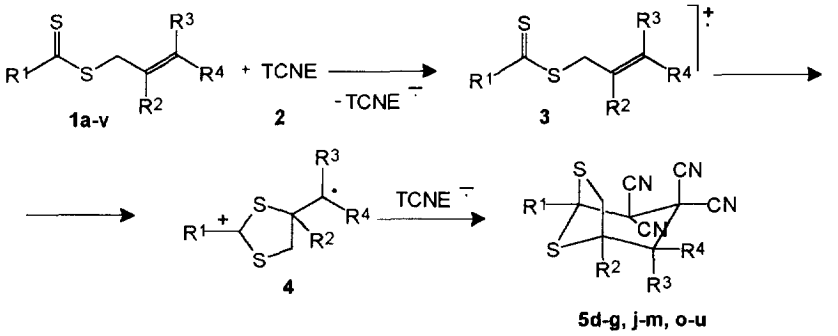
Tetracyanoethylene (TCNE) is widely used as an excellent dipolarophile in cycloaddition reactions.[1] It is known as a strong electron acceptor and therefore is capable of generating cation radicals of many organic compounds.[2] That is why the problems of donor-acceptor interaction of the reagents, the type of intermediates, such as acyclic zwitter-ions, biradicals and so on, always arise in the course of TCNE reaction mechanism investigations.[3]

Earlier we discovered a reaction of TCNE with allylic esters of dithiocarboxylic acids giving substituted 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes. The reaction mechanism, including intramolecular cyclization of the initially formed allylic ester cation radical into the five-membered cation radical **4** and the subsequent addition of the TCNE anion radical, was proposed (Scheme 1).[4]

In the present paper the reaction scope has been studied and the mechanism is proposed on the basis of the chemical behaviour of allyl dithiobenzoate (**1e**) in respect to oxidizing agents, mass-spectrometry data, the substituent effect analysis as well as by quantum chemical calculations of cation radicals of allylic esters of dithiocarboxylic acids.

RESULTS AND DISCUSSION

The reaction was conducted by refluxing a solution of allylic ester of dithiocarboxylic acid and TCNE in acetonitrile during 5-30 min, depending on the substrate. As is usually the case in single-electron reactions a large number of by-products was observed although in small amounts especially in the reactions with cinnamyl esters.



Scheme 1.

	h; R^1 = EtO	o; R^1 = $PhCH_2$
a - i; $R^2 = R^3 = R^4 = H$	i; $R^1 = Et_2N$	p; R^1 = p-O_2N-C_6H_4
a; R^1 = Me	j-n; R^1 = Ph	q; R^1 = p-Cl-C_6H_4
b; $R^1 = PhCH_2$	j; R^2 = Me, $R^3 = R^4 = H$	r; R^1 = Ph
c; R^1 = p-O_2N-C_6H_4	k; R^2 = H, $R^3 = R^4$ = Me	s; R^1 = p-Me-C_6H_4
d; R^1 = p-Cl-C_6H_4	l; R^2 = H, R^3 = H, $R^4 = CO_2Et$	t; R^1 = p-MeO-C_6H_4
e; R^1 = Ph	m; R^2 = Me, R^3 = H, $R^4 = CO_2Pr^i$	u; R^1 = EtO
f; R^1 = p-Me-C_6H_4	n; $R^2 = R^3 = R^4$ = Me	v; $R^1 = Et_2N$
g; R^1 = p-MeO-C_6H_4	o - v; $R^2 = R^3$ = H, R^4 = Ph	

The reactions of the allylic esters of dithiocarboxylic acids, unsubstituted in the allylic fragment, as substrates showed the influence of the substituents (R^1) attached to the central carbon atom of the dithioester group. For this purpose the reaction was conducted with the starting esters **1a-i** which contained both acceptor and donor substituents at the position mentioned. The reaction took place only with the compounds **1d-g**, bearing π-donor substituents. The reaction was completed in 30-40 min, but the conversion did not exceed 80 per cent. The introduction of the electron-acceptor group (p-nitrophenyl, compound **1c**) or a weak σ-donor (methyl or benzyl, compounds **1a** and **1b**, respectively) was found to inhibit the reaction. It was shown that the introduction of ethoxy or *N,N*-diethylamino groups (compounds **1h** and **1i**) leads to a mixture of unidentified products probably due to the increased capability of these electron-rich dithioesters to form oxidation products when they react with TCNE.

To investigate the influence of substituents on the allylic fragment the reaction with β- and γ-substituted allylic esters of dithiobenzoic acid, **1j-n** and **1r**, was studied.

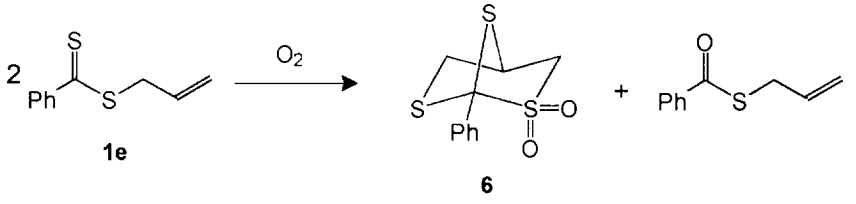
The reaction failed only in the case of the trisubstituted β,γ,γ-trimethylallyl dithiobenzoate (**1n**). This can be accounted for by unfavorable steric reasons (the formation of five neighbouring quaternary centers in a molecule of the expected reaction product). Introduction of the methyl substituent only in comparison with unsubstituted allyl dithiobenzoate did not affect the reaction time or the product yield. However, the introduction of γ-ethoxycarbonyl and especially γ-phenyl groups, stabilizing the radical center on the

neighbouring atom of the intermediate cation radical **4**, leads to an increase of conversion to 95-98 per cent and a reduction in the reaction time of 3-5 min. The reaction was conducted with cinnamyl esters of dithiocarboxylic acids which contained both acceptor and donor substituents at the central carbon atom of the dithioester group **1o-v**. The stabilization of the radical center makes the reaction proceed independently of the nature of such substituents. Thus, cinnamyl dithiophenylacetate (**1o**) and cinnamyl p-nitrodithiobenzoate (**1p**), as distinct from the corresponding allylic esters (**1b** and **1c**), react with TCNE in 5 min with high selectivity. A special note must be made of cinnamyl *p*-methoxydithiobenzoate (**1t**) and cinnamyl *O*-ethylxanthate (**1n**) in which both radical and cationic centers are strongly stabilized which is why the reaction with TCNE proceeds at room temperature. Cinnamyl *N,N*-diethyldithiocarbamate (**1v**), as well as the corresponding allylic ester (**1i**), undergoes oxidation by TCNE.

We now discuss the proposed reaction mechanism on the basis of the experimental data.

Allylic esters of dithiocarboxylic acids are weak π-donors because they possess unsaturated fragments and have ionization potentials from 9.81 (allyl p-nitrodithiobenzoate **1c**) to 8.89 eV (cinnamyl *N,N*-diethyldithiocarbamate **1v**; ionization potentials for both compounds were calculated by the MNDO method in standard parametrization). Taking into account that, in most cases, the reaction was conducted at 80 °C, the formation of cation radical **3** in the reaction of TCNE with allylic esters of dithiocarboxylic acids is quite reasonable.

We have found that 1-phenyl-2,6,7-trithiabicyclo[2.2.1]heptane 2,2-dioxide (**6**) is formed in the oxidation of allyl dithiobenzoate (**1e**) by atmosphere oxygen (Scheme 2).[5]

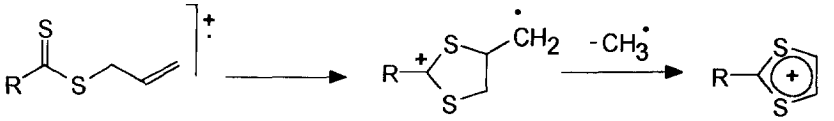


Scheme 2

The first step in the reaction is suggested to be single-electron oxidation of the initial ester by oxygen, resulting in the formation of cation radical **3e**. The molecule of compound **6** contains the same five-membered fragment as does **5e**. This suggests that the oxidation reaction also proceeds *via* a five-membered cation radical **4e**.

It is well known that in mass spectrometric studies the electron impact generates cation radicals, and these undergo further reactions, which can be studied in detail. In contrast to allyl carboxylates and *S*-allyl monothiocarboxylates which fragment similarly to ordinary esters, the main fragmentation mode of allylic dithiocarboxylates involves an unusual elimination of the γ-carbon atom of the allylic radical. This behaviour was accounted for by intramolecular cyclization of the initially formed dithioester cation radical, leading to the

distonic (in which the localizations of radical and cationic centers are not coincident) 5-membered cation radical **4** with subsequent elimination of CH_3 radical and formation of an aromatic 1,3-dithiolium ion **7** (Scheme 3).[6]



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Scheme 3.

This observation has been confirmed by us; moreover, in the EIMS of the bicyclic compounds **5** and **6** after the initial loss of TCNE and SO_2, further fragmentation follows qualitatively and almost quantitatively that found in the mass spectrum of the dithioester **1e**.

Regarding these data in the context of our investigation we came to the conclusion that they confirm the possibility of cyclization of the cation radical **3** to **4** not only in the gas-phase but also in solution.

On the basis of analysis of the substituent effects it can be supposed that we are dealing with exactly the distonic cation radical **4**.

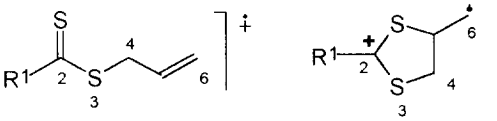
The experimental data show that the reaction is favored by electron-donor substituents at the central carbon atom of the dithioester group and by substituents at the γ-carbon atom of the allylic fragment which stabilize radical centers (CH_3, CO_2R, Ph). As a rule the stabilization of one of the reaction centers is sufficient. For instance, as mentioned above, cinnamyl *p*-nitrodithiobenzoate (**1p**) and cinnamyl dithiophenylacetate (**1o**) react with TCNE, while the corresponding allylic esters do not. The stabilization of both centers allows the reaction to take place at room temperature. The data are therefore consistent with the proposition that the anion radical TCNE reacts with the cyclic cation radical **4** only when radical and cationic centers are remote from each other and located on different atoms in the latter intermediate; that is to say distonic.[7]

We have performed quantum chemical calculations by the MINDO/3 method (in UHF approach) of the cation radicals **3a-i**, **o-u** and **4a-i**, **o-u**. The results are presented in Tables 1 and 2. Some important conclusions may be drawn from these calculations.

On electron transfer from a molecule of the allylic dithiocarboxylate to TCNE a cation radical **3** is generated in which the cationic and radical centers are localized mainly at the central carbon atom. In the case the cation radicals generated from cinnamyl esters the radical center is localized mainly on the γ-carbon of the allylic fragment.

Then the exothermic cyclization to the distonic cation radical **4** takes place; according to our calculations ΔH of this reaction is 18-30 kcal/mole. In the cyclic cation radical **4** the cationic center is localized mainly at C-2 of the dithiolane ring, while the spin density is partly localized either at the former γ-carbon atom of the allylic fragment (in which case the addition of the anion radical of TCNE is expected) or only at the atoms of the dithiolane ring (in which case the reaction fails).

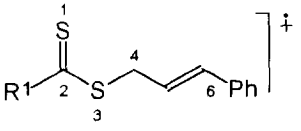
Table 1. Charge and spin density distribution for some conventional cation radicals **3a-i** and distonic cation radicals **4a-i.**



3 **4**

Compound	Charge				Spin Density				ΔH°_{f},
	C-2	S-3	C-4	C-6	C-2	S-3	C-4	C-6	kcal/mol
3a	**0.50**	-0.17	0.33	0.08	**0.29**		0.11		180.86
4a	**0.21**	-0.04	0.11	0.14		**0.42**			155.36
3b	**0.50**	-0.18	0.32	0.08	**0.28**		0.11		211.31
4b	**0.22**	-0.06	0.11	0.14		**0.41**		0.01	189.30
3c	**0.44**	-0.10	0.27	0.06	**0.26**		0.10		202.12
4c	**0.17**	-0.04	0.11	0.14		**0.41**			179.76
3d	**0.45**	-0.11	0.27	0.05	**0.25**		0.10		198.08
4d	**0.35**	-0.12	0.14	0.04	0.13	0.03		**0.08**	181.78
3e	**0.45**	-0.11	0.26	0.05	**0.25**		0.10		204.03
4e	**0.35**	-0.11	0.14	0.04	0.13	0.02		**0.08**	187.90
3f	**0.45**	-0.11	0.27	0.05	**0.25**		0.10		197.75
4f	**0.36**	-0.12	0.14	0.04	0.13	0.02		**0.08**	181.77
3g	**0.45**	-0.11	0.26	0.04	**0.26**		0.09		149.66
4g	**0.36**	-0.14	0.15	0.03	0.14	0.02		**0.09**	133.90
3h	**0.87**	-0.27	0.34	0.09	**0.11**		**0.16**		125.37
4h	**0.68**	-0.16	0.15	0.18		0.04	**0.23**		94.78
3i	**0.43**	-0.19	0.32	0.07	**0.31**		0.09		176.36
4i	**0.25**	-0.13	0.15	0.11	**0.07**	0.05	0.01	0.03	150.04

Table 2. Charge and spin density distribution for some conventional cation radicals **3o-v** and distonic cation radicals **4o-v.**



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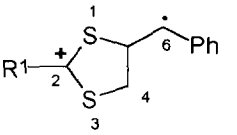

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Compound	Charge				Spin Density			ΔH°_{f},
	C-2	S-3	C-4	C-6	S-1	S-3	C-6	kcal/mol
3o	**0.47**	-0.15	0.17	0.01		0.03	**0.21**	234.20
3p	**0.47**	-0.15	0.17	0.01		0.04	**0.24**	232.22
4p	**0.42**	-0.10	0.15		0.09		**0.31**	208.96
3q	**0.48**	-0.11	0.19	0.04		0.04	**0.18**	240.97
4q	**0.42**	-0.11	0.15	-0.01	0.10		**0.32**	206.09
3r	**0.49**	-0.14	0.16	0.01		0.03	**0.21**	236.91
4r	**0.42**	-0.11	0.15	-0.01	0.10		**0.32**	212.29
3s	**0.49**	-0.14	0.16	0.01		0.03	**0.25**	231.06
4s	**0.42**	-0.12	0.15	-0.01	0.10		**0.32**	205.72
3t	**0.51**	-0.16	0.15			0.02	**0.31**	185.48
4t	**0.42**	-0.13	0.15	-0.01	0.10		**0.33**	158.58
3u	**0.76**	-0.12	0.14	0.04		0.02	**0.23**	141.60

Thus, both literature and experimental data, and quantum chemical calculations, provide supporting evidence for the first two steps of the proposed mechanism.

We propose that reaction between the distonic cation radical (**4**) and the anion radical of TCNE is the terminal step of the process.

The structures of compounds **5e**, **5o** and **5r** have been definitely determined of X-ray analysis.[8] A significant feature of these results is the configuration at position 2 of compounds **5o-u**, substituted at this position: in general, and as expected, the substitutent occupies the equatorial position in the thiacyclohexane ring, and consequently, has *endo*- configuration.

We have developed an alternative method for the determination of substituent configuration at C-7 and C-2 in these compounds.[8] This is based on the joint application of NMR spectroscopy for determination of the

coupling constants of protons at C-1, C-2, and C-7 with force field calculation for determination of torsion angles between the protons, and use of the modified Karplus equation for the calculation of the theoretical proton-proton coupling constants applying the theoretically calculated angles. The comparison of calculated and experimental coupling constants allows the unambiguous determination of the configuration of the corresponding protons and therefore of the substituents at C-2 and C-7. The accuracy of this method was confirmed for the compounds **5e**, **5o** and **5r** with known substituent configuration. Therefore the structures and configurations of all of the 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes **5** described in this paper are considered as firmly established.

CONCLUSIONS

From the above data we conclude that the scope of this reaction is limited by the necessity for the presence of either an electron-donor substituent at the dithioester central carbon atom, or, more importantly, a group stabilizing a neighbouring radical center at the γ-carbon of the allylic fragment of the dithioester **1**. The reaction takes place only with allylic esters bearing no more than two substituents in the allylic part.

The MINDO/3 method predicts the course of the reaction to a great extent and can be successfully used for the estimation of the reactivity of allylic dithiocarboxylates in the reaction with TCNE.

EXPERIMENTAL

NMR spectra were determined on a VXR-Varian-400 (400 MHz) or Brucker AC-250 MHz spectrometer with Me_4Si as internal standard. Mass spectra were determined on a Varian MAT 311A spectrometer.

Preparation of allylic esters of dithiocarboxylic acids **1a-v**. Compounds **1a**[9]; **1c**[10]; **1e**[9]; **1h-k**[9]; **1r**[9] were prepared using literature routes. Allyl dithiophenylacetate (**1b**), allyl 4-chlorodithiobenzoate (**1d**), allyl 4-methyldithiobenzoate (**1f**), allyl 4-methoxydithiobenzoate (**1g**), γ-ethoxycarbonylallyl dithiobenzoate (**1l**), γ-isopropoxycarbonyl-β-methylallyl dithiobenzoate (**1m**), β,γ,γ-trimethylallyl dithiobenzoate (**1n**), cinnamyl dithiophenylacetate (**1o**), cinnamyl 4-chlorodithiobenzoate (**1q**), cinnamyl 4-methyldithiobenzoate (**1s**), cinnamyl 4-methoxydithiobenzoate (**1t**), cinnamyl *O*-ethylxanthate (**1u**) and cinnamyl *N,N*-diethyldithiocarbamate (**1v**) were preparated adopting the procedure reported in Ref. 9, cinnamyl 4-nitrodithiobenzoate (**1p**) - in Ref. 10. All compounds were purified by column chromatography on L 100/400 silica gel eluted with hexane to yield the products as viscous red oils.

Analytical and spectroscopic data for all new dithioesters are collated in Tables 3 and 5.

Preparation of 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes **5**. *General procedure*. A solution of dithioester **1** (6 mmol) and tetracyanoethylene (6 mmol) in acetonitrile (2 ml) was refluxed for 30 min, in the case of compounds **1d-g**, **j**, **k**, or 5 min, for compounds **1l**, **m**, **o-s**, under argon. It was then allowed to cool

down and filtered. For compounds **1t** and **1u** the reaction was performed at room temperature for 30 min. The residue was recrystallised twice from acetonitrile.

The following compounds were obtained by the above procedure:
5-(4-chlorophenyl)-3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octane (**5d**): yield 30%, m.p. 211-2 °C(dec.); 3,3,4,4-tetracyano-5-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5e**): yield 53%, m.p. 224-6 °C(dec.); 3,3,4,4-tetracyano-5-(4-methylphenyl)-6,8-dithiabicyclo[3.2.1]octane (**5f**): yield 25%, m.p. 205-6 °C(dec.); 3,3,4,4-tetracyano-5-(4-methoxyphenyl)-6,8-dithiabicyclo[3.2.1]octane (**5g**): yield 45%, m.p. 193-5 °C(dec.); 3,3,4,4-tetracyano-1-methyl-5-phenyl-6,8-dithiabicyclo-[3.2.1]octane (**5j**): yield 30%, m.p. 203-5 °C(dec.); 3,3,4,4-tetracyano-2,2-dimethyl-5-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5k**): yield 42%, m.p. 220-1 °C(dec.); 3,3,4,4-tetracyano-*endo*-2-ethoxycarbonyl-5-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5l**): yield 62%, m.p. 166-7 °C(dec.); 3,3,4,4-tetracyano-*endo*-2-isopropoxycarbonyl-1-methyl-5-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5m**): yield 25%, m.p. 180-1 °C(dec.); 5-benzyl-3,3,4,4-tetracyano-*endo*-2-phenyl-6,8-dithiabicyclo-[3.2.1]octane (**5o**): yield 83%, m.p. 221-2 °C(dec.); 3,3,4,4-tetracyano-5-(4-nitrophenyl)-*endo*-2-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5p**): yield 27%, m.p. 243-4 °C(dec.); 5-(4-chlorophenyl)-3,3,4,4-tetracyano-*endo*-2-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5q**): yield 76%, m.p. 234-5 °C(dec.); 3,3,4,4-tetracyano-5,*endo*-2-diphenyl-6,8-dithiabicyclo[3.2.1]octane (**5r**): yield 70%, m.p. 222-3 °C(dec.); 3,3,4,4-tetracyano-*endo*-2-phenyl-5-p-tolyl-6,8-dithiabicyclo[3.2.1]octane (**5s**): yield 82%, m.p. 203-4 °C(dec.); 3,3,4,4-tetracyano-5-(4-methoxyphenyl)-*endo*-2-phenyl-6,8-dithiabicyclo[3.2.1]octane (**5t**): yield 84%, m.p. 177-8 °C(dec.); 3,3,4,4-tetracyano-5-ethoxy-*endo*-2-phenyl-6,8-dithiabicyclo-[3.2.1]octane (**5u**): yield 80%, m.p. 177-8 °C(dec.).

Analytical and spectroscopic data for compounds **5d-g**, **j-m**, **o-u** are collated in Tables 4 and 6.

Table 3. Analytical data for new dithioesters **1**.

Compound	Formula	Found (%) (Required)			
		C	H	N	S
1b	$C_{11}H_{12}S_2$	62.46 (63.41)	5.83 (5.80)		31.71 (30.78)
1d	$C_{10}H_9ClS_2$	52.44 (52.50)	3.94 (3.96)		28.15 (28.03)
1f	$C_{11}H_{12}S_2$	63.46 (63.41)	5.64 (5.80)		30.90 (30.79)
1g	$C_{11}H_{12}OS_2$	58.90 (58.89)	5.38 (5.39)		28.71 (28.58)
1l	$C_{13}H_{14}O_2S_2$	58.54 (58.62)	5.23 (5.30)		24.01 (24.07)
1m	$C_{15}H_{18}S_2O_2$	61.13 (61.19)	6.18 (6.16)		21.76 (21.78)
1n	$C_{13}H_{16}S_2$	66.05 (66.05)	6.63 (6.82)		27.32 (27.13)
1o	$C_{17}H_{16}S_2$	71.62 (71.78)	5.62 (5.67)		22.76 (22.55)
1p	$C_{16}H_{13}NO_2S_2$	60.85 (60.93)	4.27 (4.15)	4.47 (4.44)	20.47 (20.33)

1q	$C_{16}H_{13}ClS_2$	63.07 (63.04)	4.25 (4.30)		20.91 (21.03)
1s	$C_{17}H_{16}S_2$	71.64 (71.78)	5.68 (5.67)		22.68 (22.54)
1t	$C_{17}H_{16}OS_2$	67.85 (67.96)	5.41 (5.37)		21.32 (21.34)
1u	$C_{12}H_{14}OS_2$	61.57 (60.46)	5.99 (5.92)		26.84 (26.90)
1v	$C_{14}H_{19}NS_2$	64.01 (63.35)	7.21 (7.22)	5.23 (5.28)	23.55 (24.16)

Table 4. Analytical data for 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes **5**.

Compound	Formula	Found (%) (Required)			
		C	H	N	S
5d	$C_{16}H_9ClN_4S_2$	53.73 (53.85)	2.52 (2.54)	15.81 (15.70)	18.06 (17.97)
5e	$C_{16}H_{10}N_4S_2$	59.67 (59.61)	3.67 (3.13)	17.56 (17.38)	19.90 (19.89)
5f	$C_{17}H_{12}N_4S_2$	60.66 (60.69)	3.65 (3.60)	16.70 (16.66)	19.00 (19.06)
5g	$C_{17}H_{12}N_4OS_2$	57.62 (57.93)	3.49 (3.43)	15.65 (16.90)	18.10 (18.19)
5j	$C_{17}H_{12}N_4S_2$	59.71 (60.69)	3.56 (3.60)	16.67 (16.65)	19.05 (19.09)
5k	$C_{18}H_{14}N_4S_2$	61.65 (61.69)	4.08 (4.03)	16.66 (15.99)	18.37 (18.30)
5l	$C_{19}H_{14}N_4O_2S_2$	57.86 (57.85)	3.62 (3.58)	14.42 (14.20)	16.32 (16.26)
5m	$C_{21}H_{18}N_4O_2S_2$	59.89 (59.70)	4.34 (4.29)	13.12 (13.26)	15.05 (15.17)
5o	$C_{23}H_{16}N_4S_2$	66.99 (66.96)	3.97 (3.90)	13.77 (13.58)	15.62 (15.54)
5p	$C_{22}H_{13}N_5O_2S_2$	59.41 (59.58)	2.97 (2.95)	15.66 (15.79)	14.33 (14.46)
5q	$C_{22}H_{13}ClN_4S_2$	60.83 (61.03)	2.97 (3.03)	12.80 (12.94)	14.72 (14.81)
5r	$C_{22}H_{14}N_4S_2$	66.67 (66.31)	3.55 (3.54)	14.36 (14.06)	16.05 (16.05)
5s	$C_{23}H_{16}N_4S_2$	66.92 (66.96)	4.01 (3.91)	13.61 (13.58)	15.87 (15.54)
5t	$C_{23}H_{16}N_4OS_2$	64.26 (64.46)	3.62 (3.76)	12.91 (13.07)	14.51 (14.96)
5u	$C_{18}H_{14}N_4OS_2$	58.47 (58.99)	3.55 (3.85)	15.00 (15.29)	16.80 (17.50)

Table 5. Spectroscopic data for new dithioesters **1**.

Comp.	NMR ^1H	
	MHz, solvent	δ_H
1b	400, CD_3CN	3.86 (2 H, d, J 7 Hz, α-CH_2), 4.32 (2 H, s, CH_2Ph), 5.15 (1 H, d, J 10 Hz, γ-H^b), 5.29 (1 H, d, J 17 Hz, γ-H^a), 5.82 (1 H, m, J 7, 10 and 17 Hz, β-CH), 7.25-7.37 (5 H, m, Ph)

1d	400, $CDCl_3$	4.02 (2 H, dt, J 2 and 7 Hz, α-CH_2), 5.24 (1 H, dd, J 2 and 10 Hz, γ-H^b), 5.39 (1 H, dd, J 2 and 17 Hz, γ-H^a), 5.93 (1 H, m, J 7, 10 and 17 Hz, β-CH), 7.35 (2H, d, J 9 Hz, Ar), 7.94 (2H, d, J 9 Hz, Ar)
1f	250, $CDCl_3$	2.38 (3 H, s, CH_3), 4.05 (2 H, d, J 7 Hz, α-CH_2), 5.24 (1 H, d, J 10 Hz, γ-H^b), 5.40 (1 H, d, J 17 Hz, γ-H^a), 5.96 (1 H, m, J 7, 10 and 17 Hz, β-CH), 7.18 (2H, d, J 8 Hz, Ar), 7.96 (2H, d, J 8 Hz, Ar)
1g	250, $CDCl_3$	3.83 (3 H, s, OCH_3), 4.04 (2 H, d, J 7 Hz, α-CH_2), 5.21 (1 H, d, J 10 Hz, γ-H^b), 5.37 (1 H, d, J 17 Hz, γ-H^a), 5.94 (1 H, m, J 7, 10 and 17 Hz, β-CH), 6.86 (2H, d, J 8 Hz, Ar), 8.07 (2H, d, J 9 Hz, Ar)
1l	400, $(CD_3)_2O$	1.23 (3 H, t, J 7 Hz, CH_3), 4.14 (2 H, q, J 7 Hz, CH_2Me), 4.28 (2 H, dd, J 2 and 7 Hz, α-CH_2), 6.17 (1 H, m, J 2 and 14 Hz, γ-H), 6.94 (1 H, m, J 7 and 14 Hz, β-CH), 7.47 - 8.01 (5 H, m, Ph)
1m*	400, $CDCl_3$	*cis*: 1.25 (6 H, d, J 6 Hz, $2CH_3$), 1.99 (3 H, s, CH_3), 4.13 (2 H, s, α-CH_2), 5.04 (1 H, m, $CH(Me)_2$), 5.82 (1 H, s, γ-H), 7.36 - 7.98 (5 H, m, Ph) *trans*: 1.26 (6 H, d, J 6 Hz, $2CH_3$), 2.28 (3 H, s, CH_3), 4.72 (2 H, s, α-CH_2), 5.04 (1 H, m, $CH(Me)_2$), 5.96 (1 H, s, γ-H), 7.38 - 7.99 (5 H, m, Ph)
1n	400, $CDCl_3$	1.74 (3 H, s, Me), 1.78 (3 H, s, Me), 1.79 (3 H, s, Me), 4.05 (2 H, s, CH_2), 7.39 - 8.01 (5 H, m, Ph)
1o	250, $CDCl_3$	4.02 (2 H, d, J 7 Hz, α-CH_2), 4.32 (2 H, s, CH_2Ph), 6.20 (1 H, dt, J 7 and 16 Hz, β-CH), 6.62 (1H, d, J 16 Hz, γ-H), 7.2 - 7.4 (10 H, m, 2Ph)
1p	250, $CDCl_3$	4.22 (2 H, d, J 7 Hz, α-CH_2), 6.27 (1 H, dt, J 7 and 16 Hz, β-CH), 6.73 (1H, d, J 16 Hz, γ-H), 7.25 - 7.40 (5 H, m, Ph) 8.06 (2H, d, J 8 Hz, Ar), 8.24 (2H, d, J 8 Hz, Ar)
1q	400, DMF-D_7	4.40 (2 H, d, J 7 Hz, α-CH_2), 6.55 (1H, dt, J 7 and 15 Hz, β-CH), 6.96 (1 H, d, J 15 Hz, γ-H), 7.43 - 7.43 (5 H, m, Ph) 7.69 (2 H, d, J 8 Hz, Ar), 8.15 (2 H, d, J 8 Hz, Ar)
1s	250, $CDCl_3$	2.37 (3 H, s, CH_3), 4.22 (2 H, d, J 7 Hz, α-CH_2), 6.32 (1 H, dt, J 7 and 16 Hz, β-CH), 6.72 (1 H, d, J 16 Hz, γ-CH), 7.18 (2H, d, J 10 Hz, Ar), 7.33 (5H, m, Ph), 7.96 (2 H, d, J 10 Hz, Ar)
1t	250, $CDCl_3$	3.85 (3 H, s, OCH_3), 4.23 (2 H, d, J 9 Hz, α-CH_2), 6.31 (1 H, dt, J 9 and 18 Hz, β-CH), 6.88 (1 H, d, J 18 Hz, γ-CH), 6.88 (2 H, d, J 11 Hz, Ar), 7.36 (5 H, m, Ph), 8.11 (2 H, d, J 11 Hz, Ar)
1u	400, $CDCl_3$	1.43 (3 H, t, J 7 Hz, CH_3), 4.01 (2 H, d, J 6 Hz, α-CH_2), 4.72 (2 H, q, J 7 Hz, CH_2Me), 6.31 (1 H, dt, J 6 and 16 Hz, β-CH), 6.67 (1 H, d, J 16 Hz, γ-CH), 7.25 - 7.40 (5 H, m, Ph)
1v	400, $CDCl_3$	1.25 (6 H, t, J 7 Hz, 2 CH_3), 3.69 (2 H, q, J 7 Hz, $CH_2{}^a$Me), 4.00 (2 H, q, J 7 Hz, $CH_2{}^b$Me), 4.15 (2 H, d, J 7 Hz, α-CH_2), 6.30 (1 H, dt, J 7 and 16 Hz, β-CH), 6.60 (1 H, d, J 16 Hz, γ-CH), 7.19 - 7.36 (5 H, m, Ph)

* Mixture of *cis*- and *trans*- isomers 1 : 1.

Table 6. Spectroscopic data for 3,3,4,4-tetracyano-6,8-dithiabicyclo[3.2.1]octanes **5**.
(4H^a and 6H^a - exo-protons, 4H^b and 6H^b - *endo*-protons).

Comp.	*m/z* (Required)	NMR ^{1}H	
		MHz, solvent	δ_H
5d	356 (356)	400, DMF-D7	3.05 (1 H, dd, J 4 and 16 Hz, 4-H^a), 3.82 (1 H, dd, J 3 and16 Hz, 4-H^b), 4.00 (2 H, m, 6-CH_2), 5.00 (1 H, m, 5-H), 7.83 (2H, d, J 7 Hz, Ar) 7.89 (2H, d, J 7 Hz, Ar)
5e	322 (322)	400, DMF-D7	3.03 (1 H, ddd, J 1, 4 and 16 Hz, 4-H^a), 3.80 (1 H, dd, J 3 and 16 Hz, 4-H^b), 3.98 (1 H, ddd, J 1, 6 and 11 Hz, 6-H^a), 4.00 (1 H, dd, J 1 and 11 Hz, 6-H^b), 4.98 (1 H, m, J 3, 4 and 6 Hz, 5-H), 7.79 - 7.95 (5 H, m, Ph)
5f	336 (336)	250, DMF-D7	2.36 (3 H, s, CH_3), 3.01 (1 H, dd, J 4 and 16 Hz, 4-H^a), 3.80 (1 H, dd, J 3 and 16 Hz, 4-H^b), 3.96 (2 H, m, 6-CH_2), 4.98 (1 H, m, 5-H), 7.44 (2H, d, J 8 Hz, Ar), 7.63 (2H, d, J 8 Hz, Ar)
5g	352 (352)	250, DMF-D7	3.02 (1 H, dd, J 4 and 16 Hz, 4-H^a), 3.82 (1 H, dd, J 3 and 16 Hz, 4-H^b), 3.89 (3 H, s, OCH_3), 4.00 (2 H, m, 6-CH_2), 5.00 (1 H, m, J 4 Hz, 5-H), 7.19 (2H, d, J 8 Hz, Ar), 7.68 (2H, d, J 8 Hz, Ar)
5j	336 (336)	400, DMF-D7	1.90 (3 H, s, CH_3), 3.21 (1 H, dd, J 1.5 and 15 Hz, 4-H^a), 3.81 (1 H, d, J 1.5 and 12 Hz, 6-H^a), 3.84 (1 H, d, J 15 Hz, 4-H^b), 4.01 (1 H, d, J 12 Hz, 6-H^b), 7.65 - 7.75 (5 H, m, Ph)
5k	(350)	400, DMF-D7	1.83 (3 H, s, $CH_3{}^a$), 1.87 (3 H, s, $CH_3{}^b$), 3.95 (1 H, dd, J 6 and 12 Hz, 6-H^a), 4.18 (1 H, d, J 12 Hz, 6-H^b), 4.84 (1 H, d, J 6 Hz, 5-H), 7.67 - 7.79 (5 H, m, Ph)
5l	(394)	400, DMF-D7	1.38 (3 H, t, J 7 Hz, CH_3), 3.91 (1 H, d, J 12 Hz, 6-H^b), 4.08 (1 H, dd, J 6 and 12 Hz, 6-H^a), 4.48 (2 H, q, J 7 Hz, CH_2Me), 4.80 (1 H, m, 4-H^a), 5.42 (1 H, m, 5-H),7.65 - 7.80 (5 H, m, Ph)
5m	422 (422)	400, DMF-D7	1.40 (3 H, d, J 6 Hz, $CH_3{}^a(Pr^i)$), 1.41 (3 H, d, J 6 Hz, $CH_3{}^b(Pr^i)$), 1.92 (3 H, s, 5-CH_3), 3.82 (1 H, dd, J 1 and 12 Hz, 6-H^a), 4.45 (1 H, d, J 12 Hz, 6-H^b), 4.52 (1 H, d, J 1 Hz, 4-H^a), 5.30 (1 H, m, $CH(Pr^i)$), 7.71 (5 H, m, Ph)
5o	412 (412)	400, DMF-D7	3.59 (1 H, dd, J 5 and 11 Hz, 6-H^a), 3.75 (1 H, d, J 11 Hz, 6-H^b), 3.92 (1H, d, J 14 Hz, CH^a), 3.98 (1H, d, J 14 Hz, CH^b), 5.37 (1 H, d, J 5 Hz, 5-H), 6.22 (1 H, s, 4-H), 7.50-7.60 (5 H, m, $PhCH_2$), 7.70-7.85 (5 H, m, Ph)
5p	443 (443)	400, DMF-D7	4.17 (1 H, dd, J 5 and 12 Hz, 6-H^a), 4.56 (1 H, s, 4-H^a), 4.62 (1H, d, J 12 Hz, 6-H^b), 5.10 (1 H, dd, J 5 Hz, 5-H), 7.53-7.97 (5 H, m, Ph), 8.16 (2 H, d, J 8 Hz, Ar), 8.46 (2 H, d, J 8 Hz, Ar)

5q	432 (432)	400, DMF-D7	4.20 (1 H, dd, J 5 and 12 Hz, 6-H^a), 4.63 (1 H, s, 4-H^a), 4.67 (1 H, d, J 12 Hz, 6-H^b), 5.15 (1 H, d, J 5 Hz, 5-H), 7.60-7.97 (5 H, m, Ph), 7.86 (2 H, d, J 8 Hz, Ar), 7.97 (2H, d, J 8 Hz, Ar)
5r	398 (398)	400, DMF-D7	4.18 (1 H, m, J 1, 5 and 12 Hz, 6-H^a), 4.62 (1 H, dd, J 1 and 2 Hz, 4-H^a), 4.66 (1 H, dd, J 1 and 12 Hz, 6-H^b), 5.12 (1 H, m, J 1, 2 and 5 Hz, 5-H), 7.60-7.80 (10 H, m, 2Ph)
5s	412 (412)	250, DMF-D7	2.45 (3 H, s, CH_3), 4.18 (1 H, dd, J 6 and 14 Hz, 6-H^a), 4.60 (1 H, s, 4-H^a), 4.66 (1 H, d, J 14 Hz, 6-H^b), 5.13 (1 H, d, J 6 Hz, 5-H), 7.49 (2H, d, J 8 Hz, Ar), 7.62-7.98 (5 H, m, Ph), 7.69 (2H, d, J 8 Hz, Ar)
5t	(428)	400, DMF-D7	3.92 (3 H, s, OCH_3), 4.18 (1 H, dd, J 6 and 14 Hz, 6-H^a), 4.62 (1 H, s, 4-H^a), 4.66 (1 H, d, J 14 Hz, 6-H^b), 5.12 (1 H, d, J 6 Hz, 5-H), 7.25 (2H, d, J 9 Hz, Ar), 7.55-7.98 (5 H, m, Ph), 7.75 (2 H, d, J 9 Hz, Ar)
5u	366 (366)	400, DMF-D7	1.38 (3 H, t, J 7 Hz, CH_3), 4.13 (1 H, dq, J 7 and 10 Hz, $CH_2{}^aMe$), 4.22 (1 H, ddd, J 1, 5 and 12 Hz, 6-H^a), 4.27 (1 H, dq, J 7 and 10 Hz, $CH_2{}^bMe$), 4.45 (1 H, dd, J 1 and 12 Hz, 6-H^b), 4.61 (1 H, d, J 1 Hz, 4-H^a), 4.91 (1 H, m, 5-H), 7.60-7.95 (5 H, m, Ph)

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