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Structure and Rearrangements of 3-Iso(thio,seleno)cyanato-1,2,3-triarylcyclopropenes

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Abstract—A series of new fluctional 3-iso(thio,seleno)cyanato-1,2,3-triarylcyclopropenes was synthesized. The structure of compounds was proved by ^{1}H and ^{13}C NMR, IR, and mass spectra, and that of 3-(1,2,3-triphenylcyclopropenyl) isothiocycnate was confirmed by X-ray crystallography. In compounds under consideration by means of ^{1}H and ^{13}C NMR was discovered and investigated a fast reversible migration of isocyanato, isothiocyanato, and isoselenocyanato groups along the perimeter of the theree-membered ring proceeding according to the dissociation-recombination mechanism.

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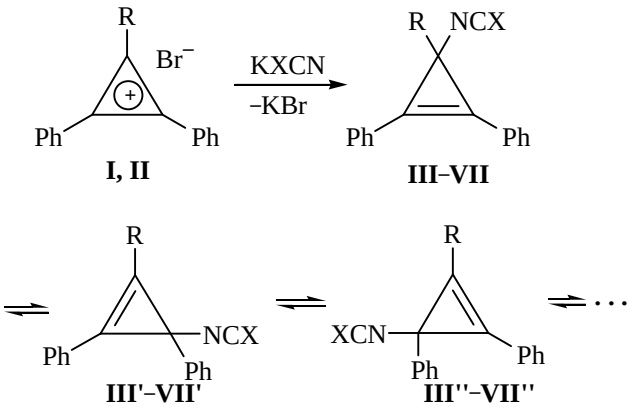
Migrations in the three-membered ring of cyclopropene were formerly found for a number of carbon- and element-centered groups (allyl [1–3], trimethylsilyl [4], azido group [5], and chlorine [6]). Aiming to study the migration ability of isocyanato, isothiocyanato, and isoselenocyanato groups we synthesized by treating triarylcyclopropenylium bromides **I** and **II** with KOCN, KSCN, and KSeCN at boiling in acetonitrile for 15 min 3-iso(thio,seleno)cyanato-1,2,3-triarylcyclopropenes **III–VII** (Scheme 1).

Scheme 1.



R = Ph (**I, III, IV, VI**), 4-MeOC$_6$H$_4$ (**II, V, VII**); X = O (**III**), S (**IV, V**), Se (**VI, VII**).

According to the data of IR and ^{13}C NMR spectroscopy and X-ray crystallography compounds **III–VII** posess covalent iso(thio,seleno)cyanate structure both in the solid state and in solution. The molecular structure of compound **IV** according to X-ray diffraction analysis proving that the molecule exists in a covalent isothiocyanate form is presented in Fig. 1.

IR spectra of isocyanates and their thio- and seleno-analogs **III–VII** lack absorption bands in the region 1400–1430 cm^{-1} characteristic of cyclopropenylium cataions; strong absorption bands in the region 1970–2250 cm^{-1} correspond to the stretching vibrations of –N=C=X groups

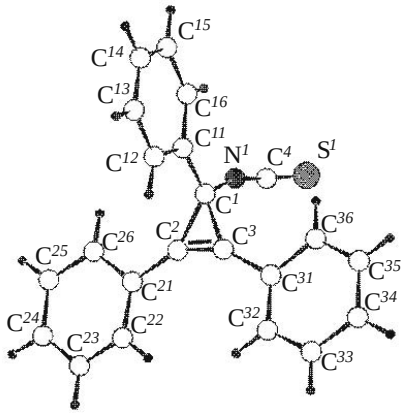


Fig. 1. Molecular structure of 3-(1,2,3-triphenylcyclopropenyl) isothiocyanate (**IV**).

(X = O, S, Se). ^{13}C NMR spectra of compounds **III–VII** give rise to signals of iso(thio,seleno)cyanate quaternary carbon atoms at δ 125.37–132.82 ppm, typical for such compounds, whereas the reported signals of carbon atoms of (thio,seleno)cyanate groups appear in the ^{13}C NMR spectra in the range 110–114 ppm [7]. The resonances of cyclopropenyl sp^3-hybridized carbons of compounds **III–VII** are observed at 45.60–48.79 ppm. This upfield shift of signals is due to the anisotropic effect of –N=C=X groups (X = O, S, Se).

^{13}C NMR spectrum of isothiocyanate derivative **IV** at room temperature together with assignment of signals is presented in Fig. 2. On heating the solution in C_6D_6 the carbon signals both of the theree-membered ring and of all the phenyl groups of compound **IV** synchronously suffer reversible broadening and coalesce at 50–80°C.

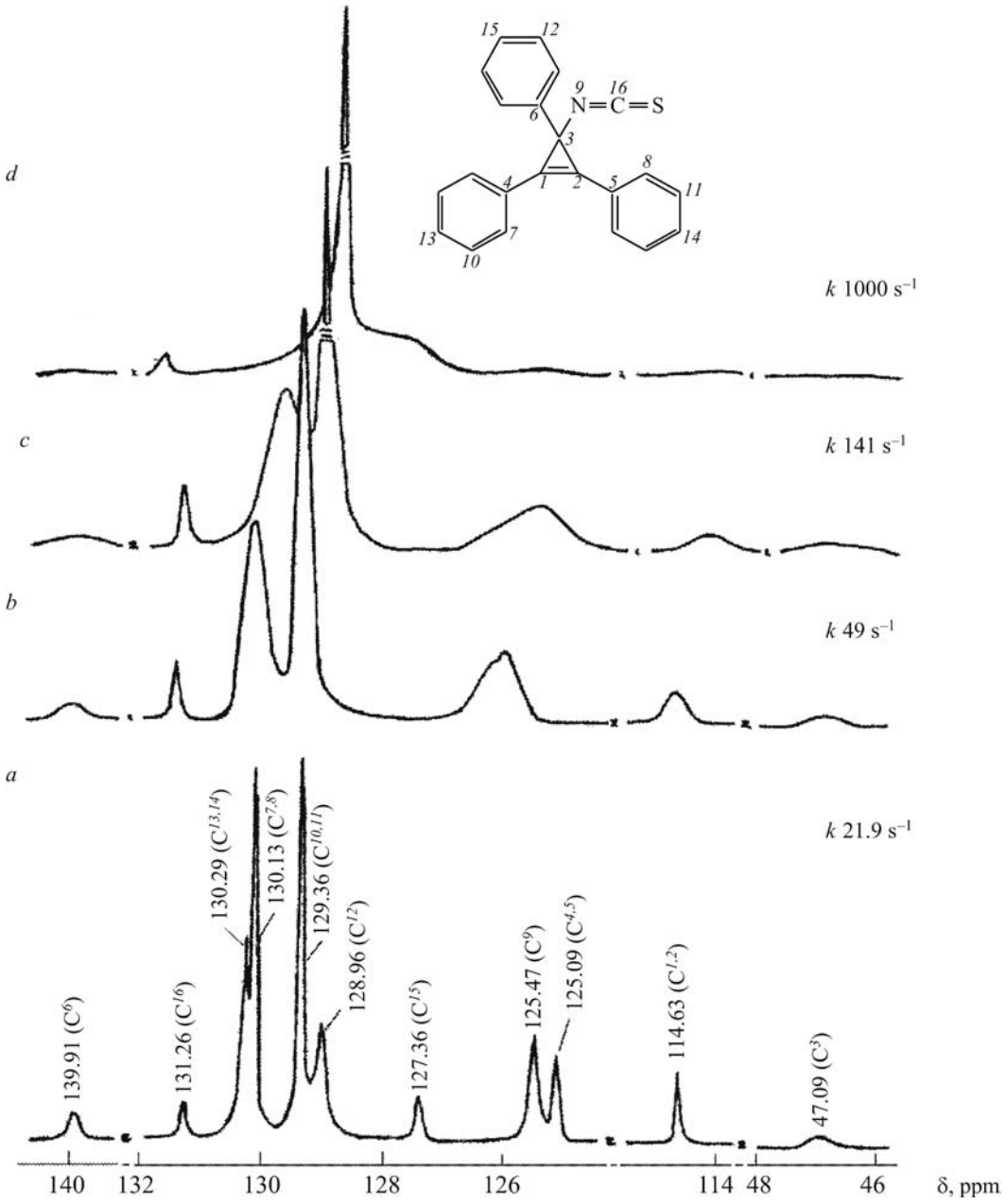


Fig. 2. ^{13}C NMR spectra (75.47 MHz) of a solution of 3-(1,2,3-triphenylcyclopropenyl) isothiocyanate (**IV**) in C_6D_6 at 25 (*a*), 35 (*b*), 49 (*c*), and 80°C (*d*). The assignment of signals was performed using monoresonance ^{13}C NMR spectra and APT procedure. Solvent signals are subtracted from the spectra.

Table 1. Kinetic and activation parameters of migration of –N=C=X groups (X = O, S, Se) in compounds **III–VII**

Compound no.	Solvent	Process type	$k_{25°C}$, s^{-1}	$\Delta G^{\neq}_{25°C}$, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.
III	$C_6D_5CD_3$	**III ⇄ III' ⇄ III''**	0.45	17.9	15.8 ± 0.4	–6.9 ± 0.6
IV	C_6D_6	**IV ⇄ IV' ⇄ IV''**	21.9	15.6	14.3 ± 0.3	–4.4 ± 0.4
IV	$CDCl_3$	**IV ⇄ IV' ⇄ IV''**	139	14.5	10.7 ± 0.3	–12.8 ± 0.4
V	$CDCl_3$	**V' ⇄ V''**	100	14.7		
		V → V'	70.9	14.9		
		V' → V	83.2	14.8		
VI	$CDCl_3$	**VI ⇄ VI' ⇄ VI''**	890	13.4	12.5 ± 0.4	–3.1 ± 0.5
VII	$CDCl_3$	**VII' ⇄ VII''**	638	13.6		
		VII → VII'	539	13.7		
		VII' → VII	755	13.5		

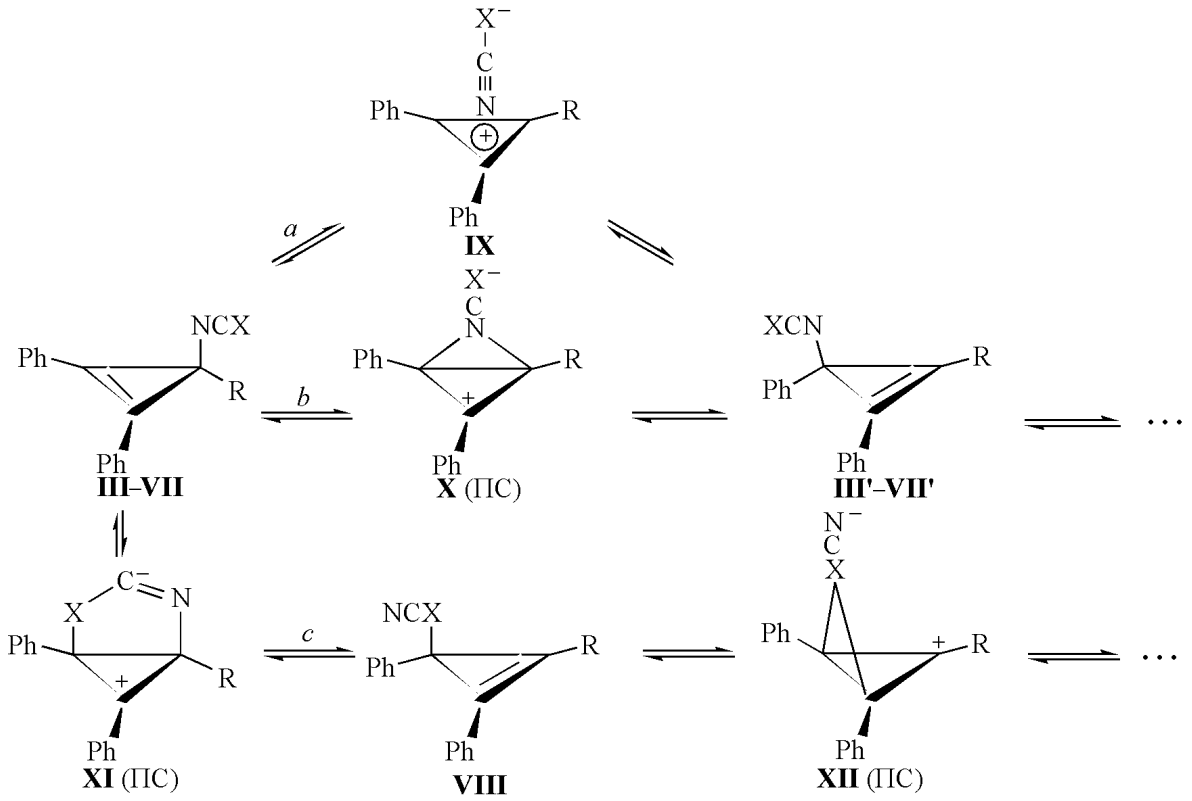
The spectra of compounds **III** and **V–VII** behave similarly.

The observed dynamic pattern of NMR spectra is due to fast reversible migration of iso(thio,seleno)cyanate groups along the perimeter of the cyclopropane ring (Scheme 1); therewith the appearance of the dynamic ^1H and ^{13}C NMR spectra does not depend on solutions concentration (0.01–0.5 mol l^{-1}) indicating the intramolecular character of the rearrangement.

From the analysis of peak form of the indicator signals in the dynamic ^{13}C NMR spectra we calculated the kinetic and activation parameters of degenerate and nondegenerate rearrangements of –N=C=X groups (X = O, S, Se) along the perimeter of triarylcyclopropene ring that are compiled in Table 1.

This rearrangement can proceed by one of three possible mechanisms described in Scheme 2.

Scheme 2.



X = O, S, Se.

Mechanism *a* involves a dissociation of C–N bond and a formation of ion pair **IX** whose recombination occurs by equiprobable covalent bonding with any of the ring carbons. According to publications [5, 6] this mechanism is the most general for cyclopropene derivatives, for their dissociation is facilitated by formation of stable aromatic cations: the migration of azido group and chlorine occurs with low activation barriers.

Mechanism *b* consists in 1,3-sigmatrope shift of NCX through a transition state **X**. The nondissociative course of reaction involving the forbidden suprasurface 1,3-sigmatrope shift is not characteristic of cyclopropene derivatives, even when they contain organometallic groups highly prone to migration by shift along the cyclopentadienyl ring. For instance, 3-(pentacarbonylrhenium)cyclopropene is a structurally rigid compound [8], and the migration of trimethylsilyl group in the 3-trimethylsilyl-3-phenyl-1,2-dimethylcyclopropene requires going over high energy barrier (~32 kcal mol^{-1}) [9].

Mechanism *c* resides in a 3,3-sigmatrope shift through an intermediate formation of (thio,seleno)cyanato isomer **VIII**. The presence of the latter (X = S) in an equilibrium with the corresponding isomers **IV** (R = Ph) or **V** (R = 4-$CH_3OC_6H_4$) was not observed in solution, but in the gas phase its presence was found in trace amounts (0.4%) by appearance of peaks with *m/z* 299 $[C_3Ph_3SCN - CN]^+$ (**IV**) or 329 $[Ph_2(CH_3OC_6H_4)C_3SCN - CN]^+$ (**V**), characteristic of fragmentaion of thiocyanate group. This mechanism was proved for a derivative of 3-allylcyclopropene [1–3]. The mechanism of 3.3-shifts was considered as an alternative to ionization-recombination for roundabout migrations of azido group in cyclopropenyl ring. An argument for this mechanism was the conversion under mild conditions of 3-azidocyclopropenes into 1,2,3-triazines [10].

The choice among the mentioned possibilities was done basing on quantum-chemical calculations by MNDO/PM3 procedure [11]. The calculations show the energetic feasibility of isothiocyanate isomer **IV** (R = Ph, X = S) compared to its thiocyanate isomer **VIII**, and also attest the higher probability of the intramolecular dissociation-recombination mechanism. The energy barrier to migration (15.4 kcal mol^{-1}) in chloroform for compound **IV** estimated as a relative energy of ion pair is well consistent with the experimental value (14.5 kcal mol^{-1}). The mechanism of dissociation-recombination is also supported by the effect of solvent polarity on the rate of group NCX migration. For instance, in compound **IV** (X = S, R = Ph) the rate of isothiocyanate group migration grew several times on going from deuterobenzene to more polar deuterochloroform (Table 1).

Table 2. Bond lengths and bond angles in compound **IV**

Bond	*l*, Å	Angle	ω, deg
S^1–C^4	1.55(2)	$C^1N^1C^4$	161.1(8)
N^1–C^1	1.47(2)	$N^1C^1C^2$	114.1(9)
N^1–C^4	1.13(2)	$N^1C^1C^3$	115.1(9)
C^1–C^2	1.51(2)	$N^1C^1C^{11}$	116.1(9)
C^1–C^3	1.53(2)	$C^2C^1C^3$	50.3(8)
C^1–C^{11}	1.46(2)	$C^2C^1C^{11}$	123.1(9)
C^2–C^3	1.29(2)	$C^3C^1C^{11}$	123.1(9)
C^2–C^{21}	1.45(2)	$C^1C^2C^3$	66.1(9)
C^3–C^{31}	1.52(1)	$C^1C^2C^{21}$	147.1(9)
C^{11}–C^{12}	1.42(2)	$C^3C^2C^{21}$	148.1(9)
C^{11}–C^{16}	1.36(2)	$C^1C^3C^2$	64.2(9)
C^{12}–C^{13}	1.40(3)	$C^1C^3C^{31}$	140.1(9)
C^{13}–C^{14}	1.32(2)	$C^2C^3C^{31}$	155.1(9)
C^{14}–C^{15}	1.39(3)	$S^1C^4N^1$	176.1(9)
C^{15}–C^{16}	1.39(2)	$C^1C^{11}C^{12}$	122.1(9)
C^{21}–C^{22}	1.37(2)	$C^1C^{11}C^{16}$	121.1(8)
C^{21}–C^{26}	1.43(1)	$C^{12}C^{11}C^{16}$	117.1(9)
C^{22}–C^{23}	1.33(2)	$C^{11}C^{12}C^{13}$	120.1(9)
C^{23}–C^{24}	1.38(2)	$C^{12}C^{13}C^{14}$	120.2(9)
C^{24}–C^{25}	1.38(2)	$C^{24}C^{25}C^{26}$	121.1(8)
C^{25}–C^{26}	1.39(2)	$C^{21}C^{26}C^{25}$	117.1(9)
C^{31}–C^{32}	1.35(2)	$C^3C^{31}C^{32}$	119.1(9)
C^{31}–C^{36}	1.42(2)	$C^3C^{31}C^{36}$	116.1(9)
C^{32}–C^{33}	1.35(1)	$C^{32}C^{31}C^{36}$	125.1(9)
C^{33}–C^{34}	1.39(2)	$C^{31}C^{32}C^{33}$	116.1(9)
C^{34}–C^{35}	1.36(2)	$C^{13}C^{14}C^{15}$	122.2(9)
C^{35}–C^{36}	1.34(2)	$C^{14}C^{15}C^{16}$	117.2(9)
		$C^{11}C^{16}C^{15}$	123.1(9)
		$C^2C^{21}C^{22}$	126.1(9)
		$C^2C^{21}C^{26}$	115.1(8)
		$C^{22}C^{21}C^{26}$	119.1(9)
		$C^{21}C^{22}C^{23}$	124.1(9)
		$C^{22}C^{23}C^{24}$	118.1(9)
		$C^{23}C^{24}C^{25}$	121.1(9)
		$C^{32}C^{33}C^{34}$	120.1(9)
		$C^{33}C^{34}C^{35}$	123.1(9)
		$C^{34}C^{35}C^{36}$	119.1(9)
		$C^{31}C^{36}C^{35}$	117.1(9)

In the series NCO < NCS < NCSe the migration ability grew on going to NCSe group; the decreased barrier to migration in the latter case was apparently due to the greater lability of system–migrant bond and higher "linearity" of the migrant making it better departing group. Thus according to microwave spectroscopy the NCX

angles in HNCX (X = O, S, Se) grow in the series NCO (172.7°) < NCS (173.8°) < NCSe (175.0°) [12].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil in a thin film. ^{1}H NMR spectra of compounds under investigation were registered on a spectrometer Bruker-AM at operating frequency 300 MHz at concentration of compounds 0.05 mol l^{-1}. ^{13}C and ^{13}C APT spectra were obtained on a spectrometer Bruker-AM at operating frequency 75.47 MHz at concentration of compounds 0.5 mol l^{-1}. Mass spectra were measured on HP 5995 A instrument with a direct admission of the sample into the ion source, ionizing energy 70 eV, 60°C.

3-Iso(thio,seleno)cyanato-1,2,3-triarylcyclopropenes (III–VII). To a solution of 4 mmol of KOCN (or KSCN, KSeCN) in 20 ml of CH_3CN was added at 24°C while vigorous stirring 4 mmol of powdered 1,2,3-triarylcyclopropenylium bromide **I** or **II** [6]. The mixture was stirred at this temperature for 30 min and then it was boiled for 15 min. The solvent was removed at reduced pressure, the solid residue was washed with water (10 × 2 ml), and dried in a vacuum-desiccator. Reaction products were twice crystallized from acetonitrile. Colorless crystals. Yields of compounds: 41 (**III**), 87 (**IV**), 85 (**V**), 62 (**VI**), 65% (**VII**).

Compound (III). mp 54–55°C. IR spectrum, cm^{-1}: 2250 (NCO), 1805 (C^1–C^3 skeletal), 1600 (C=C). ^{1}H NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 6.90–7.26 m (9H), 7.49–7.51 m (6H). ^{13}C NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 46.67 (C^3), 115.83 ($C^{1,2}$), 125.37 (NCO) 126.02, 141.31 (C^i_{arom}), 125.29, 126.62, 127.72, 128.77, 129.93, 130.20 (C_{arom}). Found, %: C 85.36; H 4.93; N 4.46. $C_{22}H_{15}NO$. Calculated, %: C 85.43; H 4.85; N 4.57.

Compound (IV). mp 141–142°C. IR spectrum, cm^{-1}: 2190–1980 (NCS), 1840 (C^1–C^3 skeletal), 1610 (C=C), 1500, 1460, 1320, 1170, 1080, 1040, 970, 920. ^{1}H NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 6.95–7.16 m (9H), 7.39–7.44 m (6H). ^{13}C NMR spectrum ($CDCl_3$, 5°C): 46.55 (C^3), 114.10 ($C^{1,2}$), 130.28 (NCS), 124.91, 139.32 (C^i_{arom}), 125.00, 127.12, 128.81, 129.14, 129.90, 129.94 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 325 $[Ph_3C_3NCS]^+ = [M]^+$ (21.9), 299 $[M - CN]^+$ (0.4), 298 $[M - HCN]^+$ (0.4), 293 $[M - S]^+$ (0.8), 292 $[M - HS]^+$ (1.1), 291 $[M — H_2S]^+$ (1.9), 267 $[M - NCS]^+$ (100), 266 $[M - HNCS]^+$ (10.2), 248 $[M - Ph]^+$ (2.3), 247 $[M - C_6H_6]^+$ (0.5), 222 $[M - PhCN]^+ = [Ph_2C_3(=S)]^+$ (5.4), 221 $[M - C_6H_6 - CN]^+$ (9.8), 214 $[M - Ph - H_2S]^+$ (1.1), 213 $[M - C_6H_6 - H_2S]^+$ (1.5), 190 $[Ph_2C_3]^+$ (3.0), 178 $[Ph_2C_2]^+$ (5.6), 115 $[PhC_3H_2]^+$ (6.0), 113 $[PhC_3]^+$ (7.7), 103 $[PhC_2H_2]^+$ (31.2), 101 $[PhC_2]^+$ (2.1), 89 $[C_7H_5]^+$ (10.9), 77 $[Ph]^+$ (14.2), 76 $[C_6H_4]^+$ (18.9), 59 $[HNCS]^+$ (4.6), 32 $[S]^+$ (4.2), 27 $[HCN]^+$ (9.3). Found, %: C 81.00; H 4.77; N 4.22; S 9.68. $C_{22}H_{15}NS$. Calculated, %: C 81.20; H 4.65; N 4.30; S 9.85.

Compound (V). mp 128–130°C. IR spectrum, cm^{-1}: 2190–1990 (NCS), 1840 (C^1–C^3 skeletal), 1620, 1610 (C=C), 1410, 1300, 1180, 1020, 860. ^{1}H NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 3.64 s (3H, OMε), 6.82–7.30 br.m (8H), 7.38–7.53 br.m (6H $_{arom}$). ^{13}C NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 45.60, 47.75 (C^3), 55.00, 55.32 (OMe), 117.51, 118.42, 119.27 ($C^{1,2}$), 128.67, 128.91 (NCS), 127.81, 128.90, 136.23, 140.30, 144.30, 158.90, 161.16 (C^i_{arom}), 115.16–132.50 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 355 $[Ph_2(CH_3OC_6H_4)C_3NCS]^+ = [M]^+$ (28.4), 340 $[M–CH_3]^+$ (4.7), 329 $[M–CN]^+$ (0.4), 328 $[M–HCN]^+$ (0.5), 324 $[M–OCH_3]^+$ (3.9), 323 $[M–S]^+$ (13.0), 314 $[M–CH_3–CN]^+$ (0.9), 313 $[M–CH_3– HCN]^+$ (1.0), 311 $[M–SC]^+$ (0.8), 310 $[M–HCS]^+$ (0.9), 309 $[M–H_2CS]^+$ (1.6), 308 $[M–CH_3S]^+$ (5.3), 307 $[M–CH_3SH]^+$ (1.5), 297 $[M–NCS]^+$ (100), 296 $[M–HNCS]^+$ (1.0), 292 $[M–CH_3O–S]^+$ (2.5), 291 $[M–CH_3O–HS]^+$ (2.4), 290 $[M–CH_3O–H_2S]^+$ (3.1), 283 $[M–NCS –CH_2]^+$ (2.7), 282 $[M–NCS–CH_3]^+$ (7.8), 281 $[M–HNCS–CH_3]^+$ (7.3), 280 $[M–NCS–CH_4]^+$ (6.7), 278 $[M–C_6H_5]^+$ (6.5), 277 $[M–C_6H_6]^+$ (4.4), 266 $[M–NCS–CH_3O]^+$ (9.7), 265 $[M–NCS–CH_3OH]^+$ (21.3), 264 $[M–HNCS–CH_3OH]^+$ (4.8), 252 $[M–C_6H_5CN]^+$ (44.3), 248 $[M–CH_3OC_6H_4]^+$ (1.3), 246 $[M–C_6H_5–S]^+$ (6.3), 237 $[M–C_6H_5–CH_3CN]^+$ (8.5), 221 $[M–CH_3OC_6H_5–HCN]^+$ (5.3), 219 $[M–C_6H_5–HNCS]^+$ (1.8), 214 $[M–CH_3OC_6H_5–H_2S]^+$ (4.8), 213 $[M–CH_3OC_6H_6–H_2S]^+$ (4.2), 209 $[M–H_3OC_6H_5≡CC_6H_5]^+$ (6.5), 190 $[Ph_2C_3]^+$ (4.6), 178 $[Ph_2C_2]^+$ (7.8), 165 $[CH_3OC_6H_4NCS]^+$ (28.9), 151 $[HOC_6H_4NCS]^+$ (11.5), 135 $[C_6H_5NCS]^+$ (14.1), 115 $[PhC_3H_2]^+$ (9.2), 113 $[PhC_3]^+$ (17.4), 108 $[CH_3OC_6H_5]^+$ (4.3), 107 $[CH_3OC_6H_4]^+$ (3.1), 77 $[Ph]^+$ (25.4), 76 $[C_6H_4]^+$ (12.2), 59 $[HNCS]^+$ (11.1), 32 $[S]^+$ (11.3), 27 $[HCN]^+$ (8.4), 15 $[CH_3]^+$ (24.2). Found, %: C 77.67; H 4.90; N 4.01; S 8.95. $C_{23}H_{17}NOS$. Calculated, %: C 77.72; H 4.82; N 3.94; S 9.02.

Compound (VI). mp 131–133°C (decomp.). IR spectrum, cm^{-1}: 1970 (NCSe), 1810 (C^1–C^3 skeletal), 1610 (C=C). ^{1}H NMR spectrum ($CDCl_3$, 5°C), δ, ppm: 7.16–7.65 br.m (15H). ^{13}C NMR spectrum ($CDCl_3$,

–20°C), δ, ppm: 46.85 (C^3), 107.75 ($C^{1,2}$), 130.10 (NCSe), 124.35, 136.96 (C^i_{arom}), 125.38, 127.13, 128.82, 129.22, 129.94, 130.35 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 372 $[Ph_3C_3NCSe]^+ = [M]^+$ (8.51), 295 $[M–C_6H_5]^+$ (1.8), 294 $[M–C_6H_6]^+$ (14.3), 293 $[M–Se]^+$ (62.2), 292 $[M–HSe]^+$ (33.2), 291 $[M–H_2Se]^+$ (14.6), 283 $[M–C_6H_5–C]^+$ (0.9), 281 $[M–CSe]^+$ (0.8), 279 $[M–H_2CSe]^+$ (1.6), 278 $[M–CH_3Se]^+$ (7.6), 277 $[M–H_3CSeH]^+$ (7.1), 269 $[M–C_6H_5CN]^+$ (2.9), 268 $[M–C_6H_6–CN]^+$ (24.5), 267 $[M–NCSe]^+$ (100), 266 $[M–HNCSe]^+$ (8.7), 216 $[M–C_6H_5–Se]^+$ (14.2), 215 $[M – C_6H_6 – Se]^+$ (3.7), 214 $[M–C_6H_6–HSe]^+$ (9.6), 190 $[Ph_2C_3]^+$ (7.3), 178 $[Ph_2C_2]^+$ (9.9), 115 $[PhC_3H_2]^+$ (4.2), 113 $[PhC_3]^+$ (3.9), 106 $[HNCSe]^+$ (4.0), 105 $[NCSe]^+$ (37.4), 89 $[C_7H_5]^+$ (7.1), 77 $[Ph]^+$ (31.6), 76 $[C_6H_4]^+$ (18.9), 51 $[C_4H_3]^+$ (33.1), 39 $[C_3H_3]^+$ (17.0), 27 $[HCN]^+$ (8.3). Found, %: C 70.88; H 4.17; N 3.66; Se 21.10. $C_{22}H_{15}NSe$. Calculated, %: C 70.97; H 4.06; N 3.76; Se 21.21.

Compound (VII). mp. 129–131°C (decomp.). IR spectrum, cm^{-1}: 1980 (NCSe), 1805 (C^1–C^3 skeletal), 1610, 1600 (C=C). ^1H NMR spectrum (C_6D_6, 5°C), δ, ppm: 3.20 s (3H) OMe, 6.89–7.10 br.m (8H), 7.34–7.54 br.m. ($6H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$, –20°C): 46.81, 48.79 (C^3), 54.20, 56.10 (OMe), 113.81, 116.01, 116.80 ($C^{1,2}$), 132.50, 132.82 (NCSe), 121.42, 127.55, 129.75, 130.30, 130.90, 137.25, 161.50 (C^i_{arom}), 124.30–130.59 (C_{arom}). Found, %: C 68.58; H 4.17; N 3.45; Se 19.52. $C_{23}H_{17}NOSe$. Calculated, %: C 68.66; H 4.26; N 3.48; Se 19.62.

X-ray diffraction analysis of 3-isothiocyanato-1,2,3-triphenylcyclopropene (IV). Crystals monoclinic. $C_{22}H_{15}NS$. *M* 325.44, space group *P* 21/*n*, *a* 13.104(5), *b* 11.644(4), *c* 12.782(5) Å, α 90, β 114.66(3), γ 90°. *V* 1772(1) $Å^3$, *Z* 4, $d_{calc.}$ 1.22 g/cm^3, *F*(000) 680. The experiments were carried out on a diffractometer Enraf Nonius CAD-4. *T* 293(2) K, MoK_α radiation, λ 0.71069 Å, θ/2θ scanning. The structure was solved by the direct method using SHEXS-97 software. Absorption μ 1.75 cm^{-1}. Scanning interval θ 1.5–20.0°; spherical segment $-12 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 12$. Reflections: 1871/1750/1087 $I(hkl) > 1\sigma(I)$. Least-squares approximation gave *R* 0.12, *Rw w* = $1/[\sigma(I)2 + (0.05F2)2]$ 0.11, ΔF_{max} 0.38 e $Å^{-3}$. Hydrogen atoms were placed into the geometrically calculated positions and refined in the *rider* approximation. Coordinates of nonhydrogen atoms and their equivalent thermal parameters are available from the authors; bond lengths and angles are presented in Table 2. The X-ray study was performed in the Federal Institute of Investigation and Testing of Materials (Berlin).

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