*ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 10, pp. 1451–1463. © Pleiades Publishing, Ltd., 2008.*
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# Theoretical and Experimental Studies on the Structure and Isomerization of Isocyano and Cyano Cyclopolyenes

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Received May 24, 2007

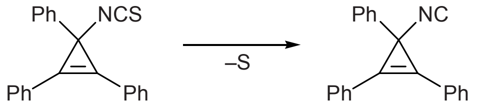
**Abstract**—Quantum-chemical calculations in terms of the density functional theory showed that cyclopolyenyl isocyanides RNC are considerably less stable than the corresponding cyanides and that they are capable of undergoing RNC→RCN isomerization according to both 1,2-shift mechanism (cyclopropenyl and cyclopentadienyl isocyanides; $\Delta E^{\neq} = 35.0$ and 37.5 kcal/mol, respectively) and previously unknown 2,5-sigmatropic shift mechanism (cycloheptatrienyl isocyanide, $\Delta E^{\neq} = 26.4$ kcal/mol). Migration of cyano group in the cyclopentadiene and cycloheptatriene systems follows the 1,5-sigmatropic shift pattern. The activation barrier to 1,5-shift of cyano group around the cycloheptatriene ring was estimated by dynamic NMR in deuterated nitrobenzene ($\Delta G^{\neq}_{190°C} = 26.5$ kcal/mol).

**DOI:** 10.1134/S1070428008100096

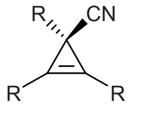
Organic cyanides and isocyanides play an important role in organic and organometallic synthesis and are used in the design of new materials and medicines. Isocyanides constitute a rare class of organic compounds in which carbon atom possesses unshared electron pair; therefore, they are widely used in coordination chemistry, e.g., for the preparation of polynuclear complexes based on isocyanoferrocene [1–3]. Taking into account the above stated, studies on the structure and properties of isocyano- and cyano-substituted cyclopolyenes as potential intermediate products for fine organic synthesis and preparation of metal complexes seem to be important. In addition, cyclopolyene derivatives in which circumambulatory migration of organic or organometallic groups is possible are now considered to be promising models of molecular motors where the mode and rate of circular motion could be controlled via proper choice of the cyclic system and migrating group [4]. Cyanocyclopolyene derivatives exist mainly as nitrile structures **I–III** [5–8].

3-Isocyano-1,2,3-triphenylcyclopropene was detected experimentally in trace amount (0.8%) in the gas phase during fragmentation of the corresponding 3-isothiocyanato derivative; the mass spectrum contained a ion peak with $m/z$ 293 $[M - \mathrm{S}]^+$ [9] (Scheme 1).

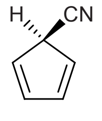
**Scheme 1.**



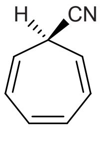
Isocyanocyclopentadiene (**V**) was reported for the first time only in 2003; it was generated from 6-azidofulvene by photolysis in methanol or pyrolysis in chloroform at 50°C; the process was accompanied by



**I**

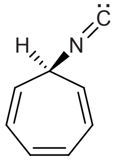


**II**

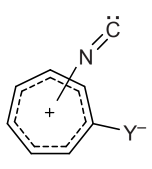


**III**

R = H, Ph.



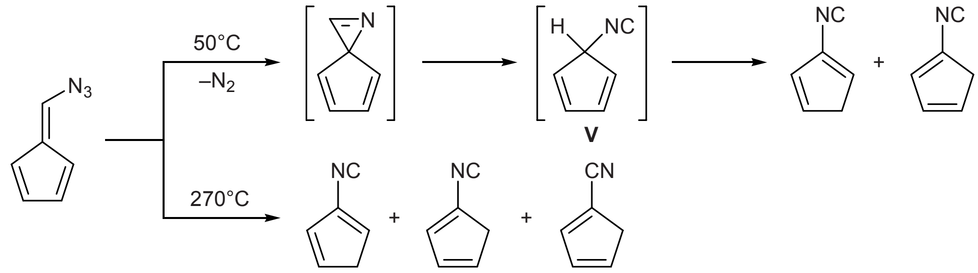
**VI**



**VIA**

Y = O, NR.

**Scheme 2.**



transformation into isomer mixture via 1,5-hydrogen shifts [5]. Flash vacuum pyrolysis of 6-azidofulvene at 270°C was shown to involve isomerization of isocyanide **V** into the corresponding cyanide in which hydrogen shifts occurred (Scheme 2).

Isocyanocycloheptatriene (**VI**) was not reported so far, though isocyanotropones and tropone imines like **VIA** were described in [10].

In the present work we performed a theoretical (DFT) study at the B3LYP/6-31G(*d*,*p*) level [11, 12] on the electronic and steric structure and relative stability of different isomers of compounds **I**–**VI** and intramolecular sigmatropic shifts and isomerizations in the series of isocyano- and cyano-substituted cyclopolyenes, as well as experimental study on previously unknown migrations of the cyano group in 7-cyanocycloheptatriene.

According to the calculations, the structures of three-, five-, and seven-membered cyano- and isocyanopolyenes **I**–**VI** correspond to minima on the potential energy surfaces (PES) and cyano isomers **I**–**III** are more stable than isocyano isomers **IV**–**VI** by 20.2, 23.2, and 20.9 kcal/mol, respectively (Table 1). We also calculated the energy barriers to the transformations of cyclopropenyl, cyclopentadienyl, and cycloheptatrienyl isocyanides **IV**–**VI** into the corresponding cyano derivatives according to different mechanisms (Table 2).

It was found that all isocyanocyclopolyenes **IV**–**VI** are converted into cyanides **I**–**III** via 1,2-shift through transition states (TS) **VII**, **IX**, and **XI** without appreciable disturbance of the ring π-system (the endocyclic double bonds are localized, and the length of the carbon–nitrogen bond in the migrating group approaches that of triple C≡N bond); the corresponding energy barriers are $\Delta E^{\neq}$ = 35.0, 37.5, and 29.9 kcal/mol, respectively (Table 2, Schemes 3–5). Figures 1–3 show the structures and geometric parameters of the transition states for all migration mechanisms.

**Table 1.** Calculated (B3LYP/6-31G**) total and relative energies of compounds **I**–**VI** and their isomers **XVIII**–**XXII** in the gas phase[a]

| Compound no. | $E_{tot}$, a.u. | $\Delta E^{\neq}$, kcal/mol | $\Delta E^{\neq}_{ZPE}$, kcal/mol | $\omega_1$, cm$^{-1}$ |
|---|---|---|---|---|
| **I** | –208.86737 | 0 | 0 | 218 |
| **IV** | –208.83475 | 20.5 | 20.2 | 190 |
| **XVIII** | –208.86918 | –1.1 | 0.8 | 200 |
| **II** | –286.34335 | 0 | 0 | 121 |
| **V** | –286.30575 | 23.4 | 23.2 | 125 |
| **XIX** | –286.35797 | –9.2 | –9.2 | 161 |
| **XX** | –286.35468 | –7.1 | –7.3 | 161 |
| **XXII** | –286.32952 | 8.7 | 8.4 | 140 |
| **III**.-*ax* | –363.75386 | 0 | 0 | 91 |
| **III**-*eq* | –363.75656 | –1.7 | –1.8 | 110 |
| **VI**-*ax* | –363.72018 | 21.1 | 20.9 | 83 |
| **XXI** | –363.76383 | –6.3 | –6.2 | 114 |

[a] Hereinafter, $E_{tot}$ is the total energy, 1 a.u. = 627.5095 kcal/mol; $\Delta E_{ZPE}$ is the relative energy calculated with account taken of zero-point harmonic vibration energy; and $\omega_1$, cm$^{-1}$, is the least harmonic vibration frequency.

**Table 2.** Calculated (B3LYP/6-31G**) total energies of transition states **VII**–**XIV** and energies of activation for the transformation of isocyano-substituted cyclopolyenes into the corresponding cyano-substituted isomers

| Transition state no. | $E_{tot}$, a.u. | $\Delta E^{\neq}_{ZPE}$, kcal/mol | $\Delta H^{\neq}$, kcal/mol | $\Delta G^{\neq}_{298}$, kcal/mol | ω,[a] $cm^{-1}$ |
|---|---|---|---|---|---|
| **VII** | –208.77636 | 35.0 | 35.0 | 35.1 | 410 |
| **VIII** | –208.68991 | 88.7 | 88.4 | 89.2 | 760 |
| **IX** | –286.24358 | 37.5 | 37.4 | 37.4 | 374 |
| **X** | –286.24179 | 38.8 | 38.4 | 39.5 | 484 |
| **XI** | –363.67010 | 29.9 | 30.3 | 28.9 | 198 |
| **XII** | –363.67690 | 26.4 | 25.6 | 27.7 | 388 |
| **XIII** | –363.60812 | 68.1 | 67.7 | 68.7 | 430 |
| **XIV**[b] | –363.70571 | 13.0 | 13.5 | 10.8 | 76 |

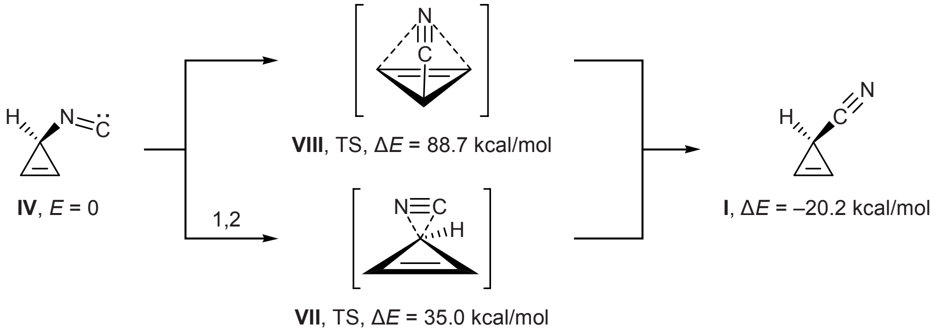
[a] ω is the only imaginary harmonic vibration frequency.

[b] Structure **VI**-*ax* (PCM, DMSO): $E_{tot}$ = –363.72821, ZPE = 0.12614 a.u.

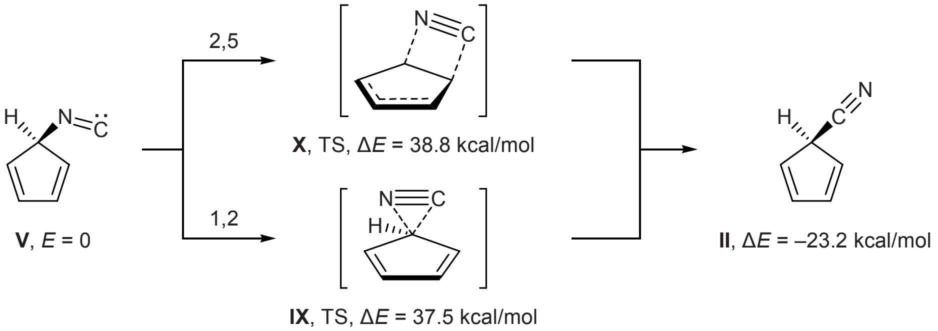
Transition states **VII** and **IX** for the cyclopropene and cyclopentadiene systems are characterized by a small charge separation between the ring and migrating group, while it is significant in TS-**XI** for the cycloheptatriene system (the total charge on the isocyano group is –0.535 *e*, and the dipole moment is μ = 7.2 D). The migrating group in TS-**XI** is remote from the ring to distances of 2.322 (N) and 2.310 Å (C), and, unlike structures **VII** and **IX**, the carbon atom therein appears above the planar seven-membered ring: the dihedral angle $CNC^7C^1$ is 70.3°; therefore, additional electrostatic interaction between the ring and migrating group is possible, which reduces the energy of TS-**XI** compared to **VII** and **IX**. The high energy barrier to alternative shift through TS-**VIII** for cyclopropenyl isocyanide (**IV**) makes this process impossible under thermal conditions (Scheme 3).

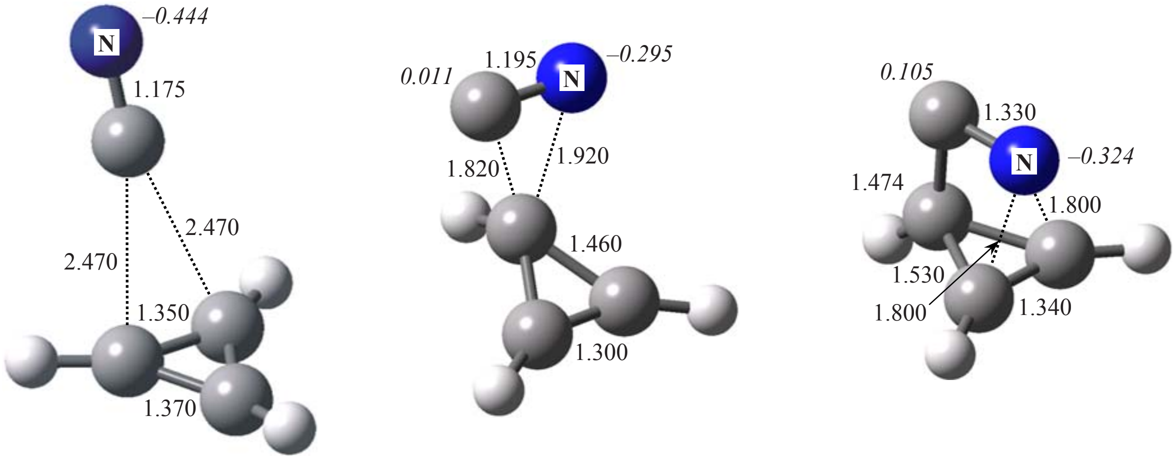
Cyclopentadienyl and cycloheptatrienyl isocyanides can also be transformed into the corresponding cyanides along a different path, 2,5-sigmatropic shift (transition states **X** and **XII**; Figs. 2, 3) with a similar energy of activation. Unlike TS-**XI**, transition states **X**

**Scheme 3.**



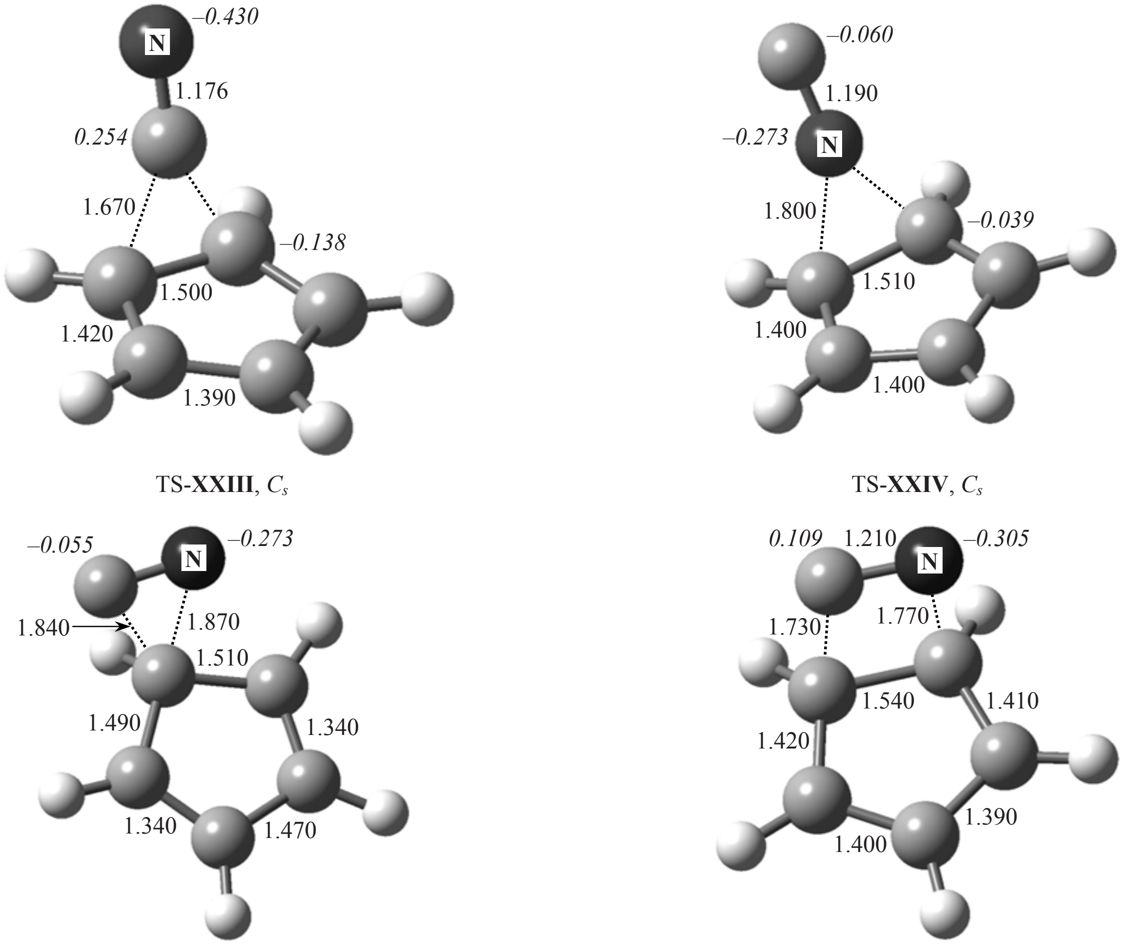
**Scheme 4.**





TS-**XVII**, $C_s$ TS-**VII**, $C_1$ TS-**VIII**, $C_1$

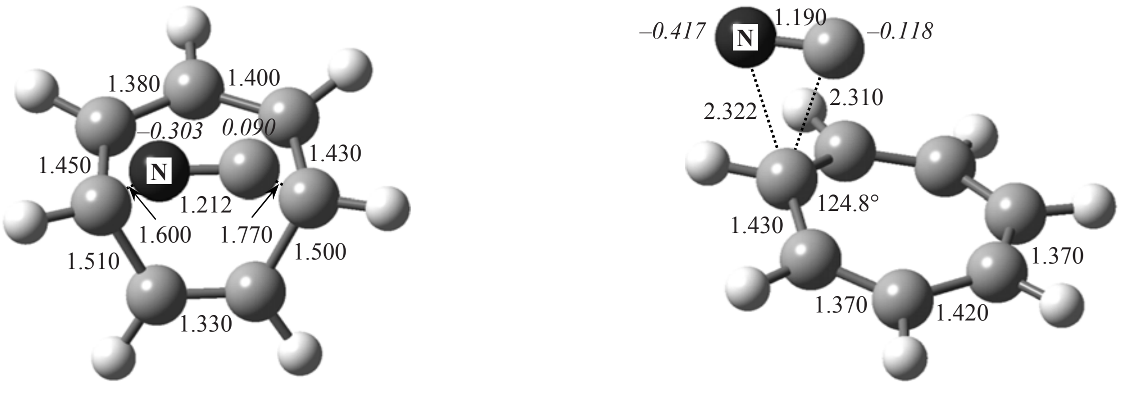
**Fig. 1.** Calculated (B3LYP/6-31G**) structures of transition states **VII**, **VIII**, and **XVII** for the CN group shifts and isocyanide–cyanide isomerization in the cyclopropene system. Interatomic distances (Å) and Mulliken charges (italicized numbers, a.u.) are given.



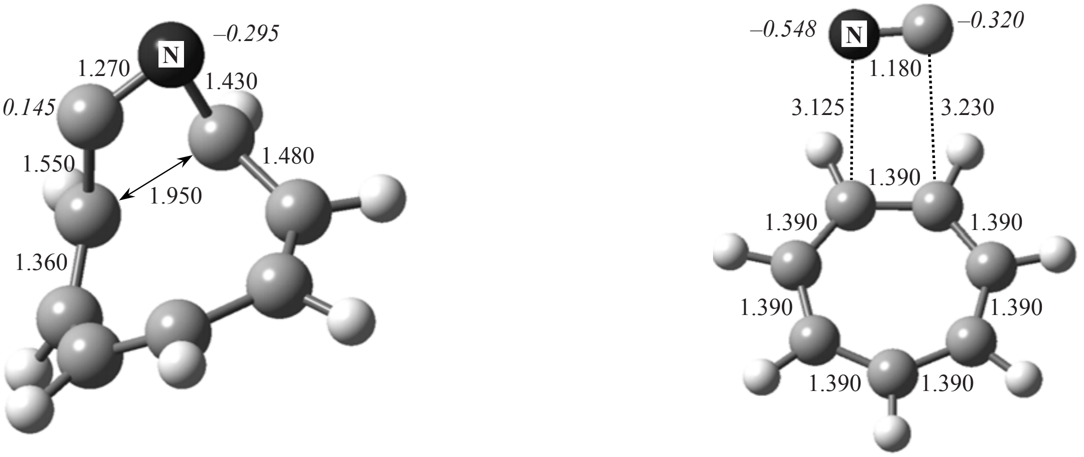
TS-**XXIII**, $C_s$ TS-**XXIV**, $C_s$

TS-**IX**, $C_1$ TS-**X**, $C_1$

**Fig. 2.** Calculated (B3LYP/6-31G**) structures of transition states **IX**, **X**, **XXIII**, and **XXIV** for shifts of cyano and isocyano groups and isocyanide–cyanide isomerization in the cyclopentadiene system. Interatomic distances (Å) and Mulliken charges (italicized numbers, a.u.) are given.



TS-**XII**, $C_1$ TS-**XI**, $C_1$



TS-**XIII**, $C_1$ **XIV**, $C_1$ (DMSO)

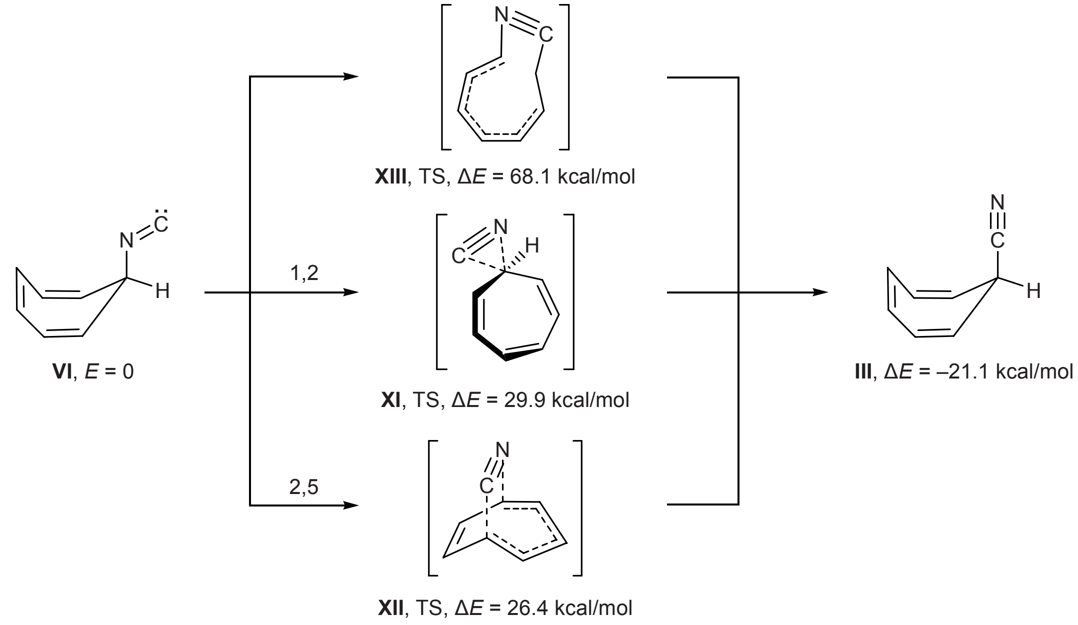
**Fig. 3.** Calculated (B3LYP/6-31G**) structures of transition states **XI**–**XIV** for the isocyanide–cyanide isomerization in the cycloheptatriene system in the gas phase and DMSO solution. Interatomic distances (Å) and Mulliken charges (italicized numbers, a.u.) are given.

and **XII** are characterized by close arrangement of the ring and migrating group and by a weak charge separation. Thus cyclopentadienyl isocyanide is capable of being converted into cyanide **II** along two paths with similar energy barriers (TS-**IX**, TS-**X**; Scheme 4). The 2,5-sigmatropic shift in the cycloheptatriene system (TS-**XII**) was found to be the lowest-energy process among the examined ones ($\Delta E^{\neq}$ = 26.4 kcal/mol). In contrast to **XI**, transition state structure **XII** is not strained; the seven-membered ring therein is not planar: two double-bonded carbon atoms deviate from the plane formed by the remaining five carbon atoms, while the latter participate in electron density delocalization. 2,5-Sigmatropic shifts have not been described in earlier experimental and theoretical studies.

Analysis of the potential energy surface for the isomerization of cycloheptatrienyl isocyanide **VI** into cyanide **III** revealed one more path involving rupture of C–C bond in the seven-membered ring and subsequent ring closure via formation of new C–C bond (TS-**XIII**); however, high energy barrier to this process makes it noncompetitive (Scheme 5, Table 2). The heights of the energy barriers to the reverse processes (cyanide → isocyanide) indicate their low probablity.

We previously performed calculations on the isomerization of methyl isocyanide into acetonitrile and found that the process involves formation of a π-complex like structures **VII**, **IX**, and **XI** [13]. As shown in [14], rearrangements of primary, secondary, and tertiary alkyl, substituted benzyl, methoxycarbonylmethyl, and triphenylmethyl isocyanides into the corresponding cyanides in such nonpolar solvents as dodecane and mesitylene are characterized by activation barriers $\Delta G^{\neq}_{250°\mathrm{C}}$ ranging from 35 to 37 kcal/mol; i.e., the nature of the fragment linked to the isocyano group weakly affects the process. This was rationalized in terms of formation of a tight hypervalent three-membered cyclic transition state.

**Scheme 5.**



Conjugated cyclopolyenes give rise to alternative isomerization paths, among which 2,5-sigmatropic shift turned out to be the most probable process for the cycloheptatriene system with three double bonds in the ring. The calculated activation barrier to 2,5-sigmatropic shift is $\Delta E^{\neq}$ = 26.4 kcal/mol (for the gas phase), indicating that isocyanide **VI** can be converted into cyanide **III** in several hours at room temperature. Insofar as the reaction of cycloheptatrienyl bromide with KCN was carried out in strongly polar media [15] and the only product was cyanide **III**, the energy barrier to the isomerization **VI** → **III** was calculated for the DMSO medium in terms of the polarization continuum model (PCM). The barrier along the 2,5-signatropic shift path was almost similar ($\Delta E^{\neq}$ = 27.1 kcal/mol, DMSO), while that corresponding to the 1,2-shift was considerably lower (TS-**XIV**, $\Delta E^{\neq}$ = 13.0 kcal/mol, DMSO, $\Delta\Delta E^{\neq}$ = 16.9 kcal/mol; Table 2). The calculated enthalpy of activation ($\Delta S^{\neq}$ = 9.1 e.u., TS-**XIV**) is fairly large and positive, which is typical of ion pair-like transition states. The structure of TS-**XIV** (Fig. 3) is characterized by very strong charge separation between the seven-membered ring and the isocyano group (–0.874 a.u. on NC), large dipole moment ($\mu$ = 20.0 D), and long distance between the ring carbon atoms and NC group. The total energy of structure **XIV** is less than the sum of the energies of tropylium cation (**XV**, $E_{\text{tot}}$ = –270.75760 a.u.) and cyanide ion (**XVI**, $E_{\text{tot}}$ = –92.94626 a.u.) in DMSO. The low calculated barrier to the isomerization **VI** → **III** in polar solvents is likely to be responsible for the fact that cycloheptatrienyl isocyanide (**VI**) could not be isolated in polar solvents.

Migrations of the cyano group and competing hydrogen shifts were found experimentally for some cyano-substituted benzocyclopolyenes [6, 16, 17]. Our experiments revealed previously unknown circumambulatory migration of the cyano group in 7-cyanocycloheptatriene (**III**) having no other substituents on the ring. With a view to elucidate possible mechanisms of such rearrangements we analyzed different paths of migration of cyano and isocyano groups around the ring in three-, five-, and seven-membered cyclic polyenes.

Rearrangements in cyclopolyene systems can follow several paths. Cyanocyclopropene can undergo rearrangements via 1,3-sigmatropic shifts of the cyano group or dissociation of the C–C bond with formation of ion pair; recombination of the latter could involve equally probable covalent bonding with any ring carbon atom (random mechanism). Five- and seven-membered systems give rise to greater diversity of possible migration mechanisms, including 1,3-, 1,5-, and 1,7-sigmatropic shifts of the cyano group and random mechanism. In addition, concurrent 1,*j*-sigmatropic shifts of hydrogen may occur.

According to the results of quantum-chemical calculations, 1,3-sigmatropic shifts of the cyano group in unsubstituted cyanocyclopropene in the gas phase require high energy ($\Delta G_{298}$ = 70.2 kcal/mol) (Scheme 6,

**Table 3.** Calculated (B3LYP/6-31G**) total energies of transition states **XVII**, **XXIII**, **XXV**, **XXVI**, **XXVIII**, and **XXX** and energies of activation for shifts of the cyano group and hydrogen atoms in cyano-substituted cyclopolyenes

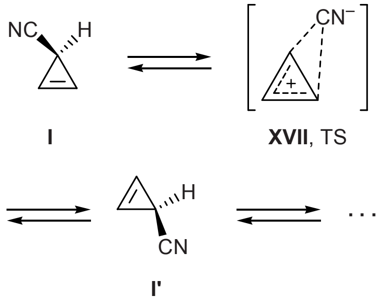
| Transition state no. | $E_{tot}$, a.u. | $\Delta E^{\neq}_{ZPE}$, kcal/mol | $\Delta H^{\neq}$, kcal/mol | $\Delta G^{\neq}_{298}$, kcal/mol | ω,[a] $cm^{-1}$ |
|---|---|---|---|---|---|
| **XVII** | –208.74790 | 72.2 | 72.9 | 70.2 | 603 |
| **XXIII** | –286.28683 | 34.4 | 34.1 | 34.9 | 676 |
| **XXVI** | –363.67125 | 49.9 | 50.5 | 47.8 | 394 |
| **XXV** | –363.69229 | 37.4 | 36.8 | 38.3 | 432 |
| **XXVIII** | –363.69989 | 32.5 | 32.2 | 32.9 | 1489 |
| **XXX**[b] | –455.92181 | 32.4 | 32.1 | 33.5 | 456 |

[a] ω is the only imaginary harmonic vibration frequency.

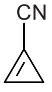
[b] **XXIX**: $E_{tot}$ = –455.97549, ZPE = 0.12448 a.u.

Table 3) and are forbidden by the symmetry rules. Figure 1 shows the structure of polar transition state **XVII** for this process, which is characterized by appreciable charge separation (–0.63 a.u. on the migrating CN group), long distance (2.470 Å) between the ring and the CN group, and hence large dipole moment (μ = 8.8 D).

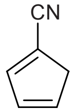
**Scheme 6.**



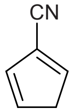
Isomeric cyanocyclopropenes **I** and **XVIII** in which the CN group is attached, respectively, to $sp^3$- and $sp^2$-hybridized carbon atoms are similar in stability ($\Delta E_{ZPE}$ = 0.8 kcal/mol), whereas more stable isomers of cyanocyclopentadiene and cyanocycloheptatriene have structures **XIX**–**XXI** ($\Delta E_{ZPE}$ = 6–9 kcal/mol) where the cyano group is attached to $sp^2$-hybridized carbon atom; these structures can be formed via hydrogen shifts (Table 1). The energy of cyclopentadienylidenemethylidenamine (**XXII**) having an NH group ($\Delta E_{ZPE}$ = 8.4 kcal/mol, Table 1) is also similar to that of cyanocyclopentadiene **II**. In fact, compounds **XIX**–**XXI** were isolated as individual substances [5, 6], and structural analog of isomer **XXII** was reported for pentacyanocyclopentadiene [18]; it exists in the polymeric form with N–H···N hydrogen bonds [19].



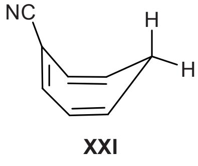
**XVIII**



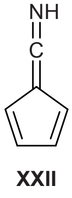
**XIX**



**XX**



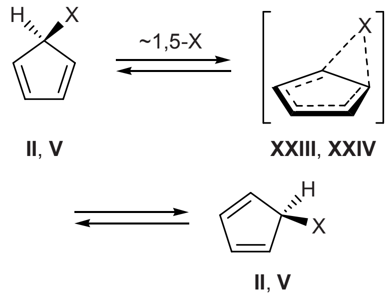
**XXI**



**XXII**

The calculated structures of transition states for 1,5-sigmatropic shifts of cyano and isocyano groups in cyclopentadiene (Scheme 7; Fig. 2; Tables 3, 4), which are allowed by the orbital symmetry rules, are typical of sigmatropic shifts: the charge separation between the ring and migrating group is insignificant, and the distances between the ring and migrating group are 1.670 (**XXIII**) and 1.800 Å (**XXIV**).

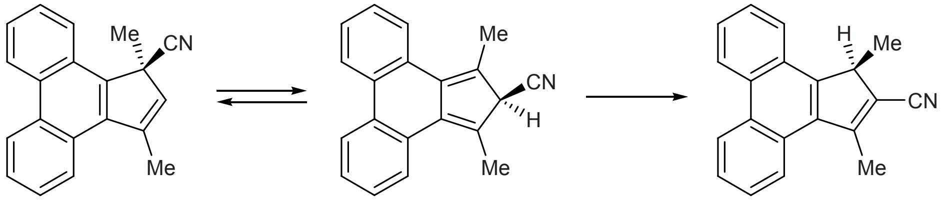
**Scheme 7.**



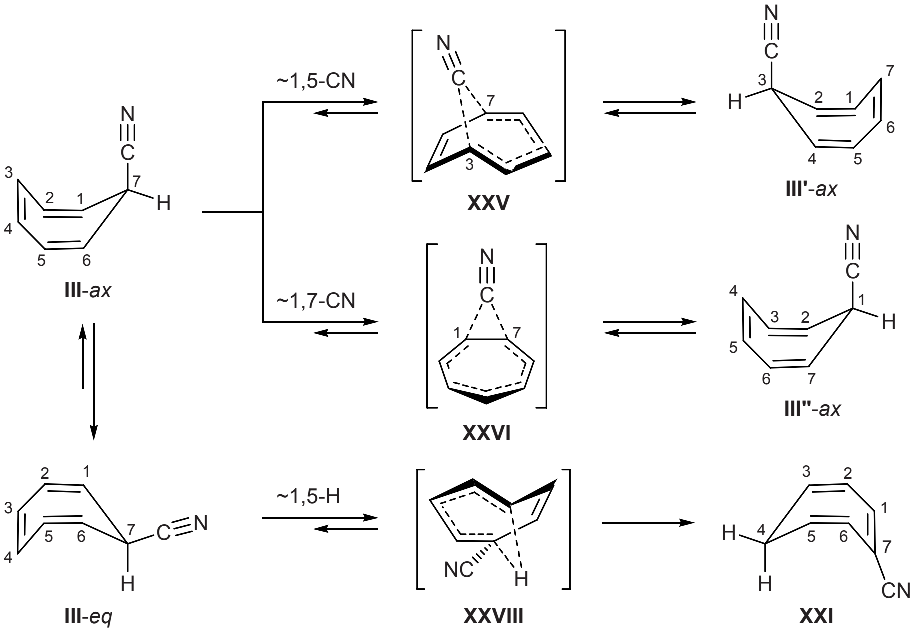
**II**, **XXIII**, X = CN; **V**, **XXIV**, X = NC.

The calculated energies of activation for cyano group migration (Table 3) approach those found experimentally for analogous migration in the 1,3-dimethyldibenzo[*e*,*g*]indene system (Scheme 8), where the rate constant of the overall process including shifts of the CN group and H-shift is $k = 19.0 \times 10^{-5}$ $s^{-1}$ in

**Scheme 8.**



**Scheme 9.**



diphenyl ether at 250°C ($\Delta G^{\neq}_{250°C}$ = 40.1 kcal/mol); i.e., it exceeds those reported for 1,3-dimethylindenes by about 2 orders of magnitude [16, 17].

Probable paths of migration of the cyano group in compound **III** were revealed by DFT calculations; in addition, paths of migration of the isocyano group in **VI** were calculated for comparison. The results showed (Table 1) that the energy difference $\Delta E_{ZPE}$ between possible conformers **III**-*eq* and **III**-*ax* with equatorial and axial orientation of the cyano group is 1.8 kcal/mol, which is very consistent with the experimental data ($\Delta G^0_{-155°C}$ = 0.8 kcal/mol) [20]. Suprafacial migrations of the CN group in **III**-*ax* and suprafacial hydrogen shifts in **III**-*eq* are possible (Scheme 9).

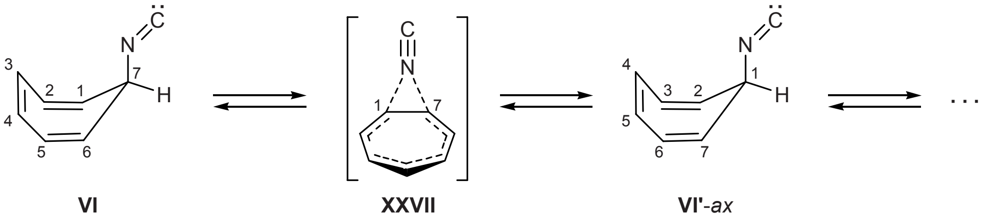
Analysis of the potential energy surfaces for migrations of cyano and isocyano group in the seven-membered ring revealed transition states for 1,5-sigmatropic shifts of the cyano group (**XXV**) and 1,7-sigmatropic shifts of the cyano (**XXVI**) and isocyano groups (**XXVII**) (Tables 3, 4; Schemes 9, 10; Fig. 4). Allowed 1,5-sigmatropic shifts (according to the Woodward–Hoffmann rules) of the cyano group in cyanocycloheptatriene are more energetically favorable than the corresponding 1,7-sigmatropic shifts by 12.5 kcal/mol, and their energies of activation approach those calculated for cyanocyclopentadiene (**II**). This may be rationalized in terms of the structure of transition state **XXV** for 1,5-shifts, where two ring carbon atoms devi-

**Table 4.** Calculated (B3LYP/6-31G**) total energies of transition states **XXIV** and **XXVII** and energies of activation for shifts of the isocyano group in isocyano-substituted cyclopolyenes

| Transition state no. | $E_{tot}$, a.u. | $\Delta E^{\neq}_{ZPE}$, kcal/mol | $\Delta H^{\neq}$, kcal/mol | $\Delta G^{\neq}_{298}$, kcal/mol | ω,[a] cm$^{-1}$ |
|---|---|---|---|---|---|
| **XXIV** | –286.23035 | 45.9 | 45.8 | 46.0 | 774 |
| **XXVII** | –363.66751 | 31.3 | 31.8 | 29.8 | 185 |

[a] ω is the only imaginary harmonic vibration frequency.

**Scheme 10.**

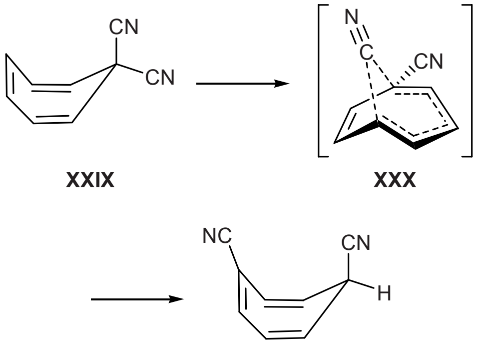


ate by an angle of 67.9° from the plane formed by the remaining five carbon atoms; as a result, they are not involved in delocalization of π-electron density. Structure **XXV** is characterized by insignificant charge separation between the ring and migrating group, and the corresponding distance is 1.701 Å (Fig. 4).

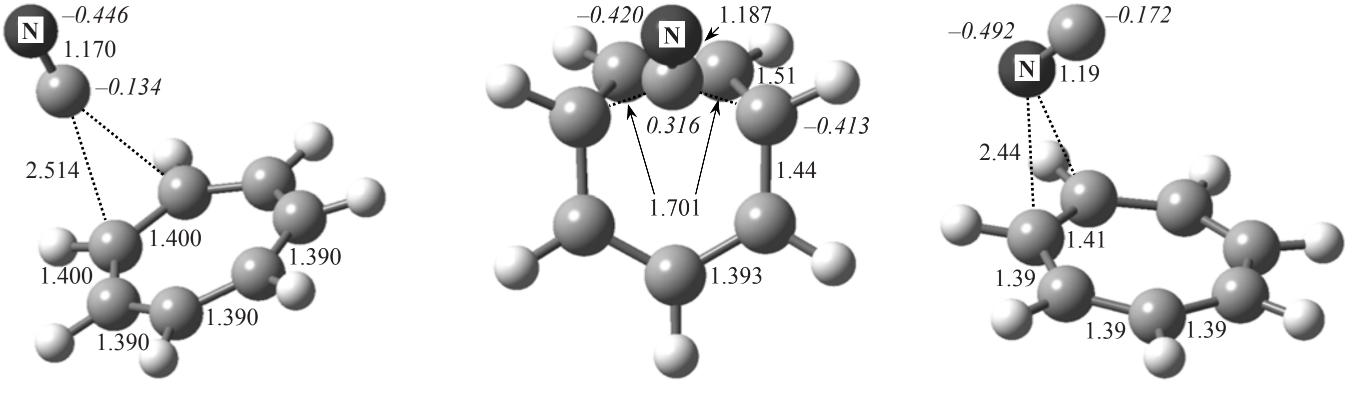
Comparison of the calculated gas-phase energy barriers (Table 3) with the experimental value determined in deuterated nitrobenzene ($\Delta G^{\neq}_{190°C}$ = 26.5 kcal/mol) counts in favor of 1,5-sigmatropic shift. Somewhat larger height of the calculated barrier suggests specific effect of such solvent as $C_6D_5NO_2$ on the rate of migration; PCM calculations give a value which is lower by only 1.2 kcal/mol ($MeNO_2$, $\Delta E^{\neq}$ = 36.2 kcal/mol). In fact, the results of additional calculations on the 1,5-CN shifts in dicyanocycloheptatriene **XXIX** [$\Delta G^{\neq}_{298}$(gas) = 33.5 kcal/mol, TS-**XXX**; Table 3] are in good agreement with the experimental data ($\Delta G^{\neq}_{298}$ = 31.0 kcal/mol in chloroform) [6] (Scheme 11).

1,5-Sigmatropic shift of the CN group in cyano-substituted benzoheptene is observed at 130–160°C ($C_6D_6$, $\Delta H^{\neq}$ = 27.2 kcal/mol, $\Delta S^{\neq}$ = –12.7 e.u.) [17] and is accompanied by 1,5-H shift; furthermore, in going from benzene to methanol the rate of migration increases only twofold, which provides a support for the concerted mechanism of the process and is consistent with the calculated data. The calculated energy barrier $\Delta G^{\neq}_{298}$ for suprafacial 1,5-hydrogen shifts in isomer **III**-*eq* is 32.5 kcal/mol (TS-**XXVIII**, Scheme 9, Table 3), i.e., it is similar to that calculated for the 1,5-CN shifts, indicating that these processes may compete with each other. This conclusion does not contradict the experimental data [6].

**Scheme 11.**



According to the orbital symmetry conservation rules, 1,7-sigmatropic shifts of isocyano group in the cycloheptatriene system are forbidden (Table 3, 4). The calculated rate of 1,7-NC shift is much higher than that of the 1,7-CN shift (the energy of activation is lower by 18.5 kcal/mol), in contrast to 1,5-shifts in the cyclo-



TS-**XXVI**, $C_s$ TS-**XXV**, $C_s$ TS-**XXVII**, $C_s$

**Fig. 4.** Calculated (B3LYP/6-31G**) structures of transition states **XXV**–**XXVII** for shifts of cyano and isocyano groups in the cycloheptatriene system. Interatomic distances (Å) and Mulliken charges (italicized numbers, a.u.) are given.

pentadiene system. In the latter case, the energy barrier to migration of isocyano group is higher by 11.5 kcal × $mol^{-1}$ than the energy barrier to migration of cyano group). While considering the calculated geometric parameters of transition states for the 1,7-shifts, strong charge separation between the planar seven-membered ring and migrating group (–0.582 a.u. on CN and –0.664 a.u. on NC), long distances between the ring and migrating group (2.514 Å in **XXVI** and 2.440 Å in **XXVII**), and large dipole moments (9.4 and 9.2 D for TS-**XXVI** and TS-**XXVII**) must be noted. Structures **XXVI** and **XXVII** differ by dihedral angles $C^7C^1CN$ and $C^7C^1NC$ (132.6 and 99.5°, respectively). It follows that the isocyano group in TS-**XXVII** hangs over the cycloheptatriene ring (Fig. 4), providing the possibility for additional interaction between π-orbitals of the ring and migrating group, which should stabilize the transition state. As shown in previous theoretical studies, just 1,7-shifts forbidden by the Woodward–Hoffmann rules are typical of migrations of chlorine [21] and $BAlk_2$ groups [22] in the cycloheptatriene system. This was rationalized in terms of Coulomb interaction between the system and migrating atom in the first case [21] and Möbius type interaction in the second [22].

Previously, migrations of various substituents around the seven-membered ring in $\eta^1$-cycloheptatriene compounds were studied by experimental methods. It was shown that their energy barriers change over a wide range, depending mainly on the nature of the central atom in the migrating group. For example, high-energy 1,5-sigmatropic shifts of hydrogen [23, 6] and methoxy group [6], relatively fast 1,5-shifts of $Ph_3Sn$ [4, 24], $Me_3Sn$ [22], and PhS groups [25], 1,7-sigmatropic shifts of ruthenium [26] and rhenium residues [27], chlorine atom [21], and $Pr_2B$ group [22], 3,3-displacement of azido group accompanied by its 1,7-sigmatropic shifts [28], fast 3,7-hetero-Cope rearrangements of SC(R)=S groups [23, 29], and shifts of NCO [30, 31], NCS [30, 31], NCSe [23, 31], and phthalimido groups [32] according to the random mechanism were described.

7-Cyanocyclohepta-1,3,5-triene (**III**) was synthesized by us from tropylium bromide and potassium cyanide according to the procedure reported in [15]. The $^1H$ and $^{13}C$ NMR data showed that compound **III** has covalent structure where the cyano group is attached to the $sp^3$-hybridized carbon atom in the seven-membered ring. The $^1H$ and $^{13}C$ NMR spectra of **III** were similar to those reported for $\eta^1$-cycloheptatriene derivatives $C_7H_7SC(OEt)=S$ [29] and $C_7H_7SnPh_3$ [24] with the difference that the 7-H (δ 2.39 ppm, t) and $C^7$ signals ($\delta_C$ 29.65 ppm) of **III** appeared in a stronger field. The observed upfield shift is likely to be related to the presence of electron-withdrawing cyano group in position *7* of molecule **III**.

Taking into account the $C_s$ symmetry of molecule **III**, its $^1H$ NMR spectrum contained four multiplets from protons in the cycloheptatriene ring. The most upfield triplet with an intensity corresponding to one proton was assigned to 7-H, and the other three signals [δ, ppm: 4.84 m (1-H, 6-H), 5.73 m (2-H, 5-H), and 6.23 m (3-H, 4-H)] were assigned by analysis of the $^1H$–$^1H$ coupling constants using the double resonance technique (successive irradiation at a resonance frequency of each proton, leading to change in the multiplicity of signals of the other protons). In keeping with the $^1H$ NMR data, 7-cyanocyclohepta-1,3,5-triene (**III**) exists mainly as a *boat* conformer with quasiequatorial orientation of the cyano group. This follows from the coupling constant between 7-H and 1(6)-H ($^3J$ = 6.15 Hz), which considerably differs from the corresponding coupling constant for triphenylstannyl derivative of cycloheptatriene ($C_7H_7SnPh_3$, $^3J_{1,7}$ = 8.0 Hz) where quasiaxial orientation of the $Ph_3Sn$ group was determined by X-ray analysis [24].

Bushweller et al. [20] found by dynamic $^1H$ NMR spectroscopy that 7-cyanocyclohepta-1,3,5-triene (**III**) exists as two rapidly interconverting (via ring inversion) *boat* conformers with quasiequatorial (**III**-*eq*) and quasiaxial (**III**-*ax*) orientation (Scheme 9). In the $^1H$ NMR spectrum (60 MHz, $CH_2CHCl$) recorded at –155°C, conformers **III**-*eq* and **III**-*ax* are observed separately at a ratio of 28:1 ($\Delta G^0_{-155°C}$ = 0.78 kcal × $mol^{-1}$), while their signals coalesce at –120°C and become narrower on further raising the temperature; the activation barriers $\Delta G^{\neq}_{-120°C}$ for the interconversion were estimated at ~8 (**III**-*eq*→**III**-*ax*) and ~9.5 kcal × $mol^{-1}$ (**III**-*ax*→**III**-*eq*). The authors believed that the conformer ratio weakly depends on the temperature, for the Gibbs entropy of activation in such processes is close to zero. No signals assignable to norcaradiene isomer were detected in the $^1H$ NMR spectrum of cycloheptatriene **III**.

The $^1H$ NMR spectra of 7-cyanocycloheptatriene **III** showed temperature dependence in the range from 120 to 180°C (nitrobenzene-$d_5$): reversible asynchronous broadening of signals from protons in the cycloheptatriene ring was observed. Here, the 7-H and 3(4)-H signals turned wider first, and then the others became broader. In the 2D (EXSY) $^1H$ and $^{13}C$ NMR spectra of 7-cyanocyclohepta-1,3,5-triene (**III**) (Fig. 5) cross peaks corresponding to 7–3,4, 3,4–1,6, and 1,6–2,5 correlations appeared at 120°C. This spectral pattern results from intramolecular circumambulatory 1,5-sigmatropic migration of the cyano group (Scheme 9). Analysis of the shape of signals in the dynamic $^1$H NMR spectrum of cyanocycloheptatriene **III** allowed to estimate the energy barrier $\Delta G^{\neq}_{190°C}$ to the cyano group shift at 26.5 kcal/mol (nitrobenzene-$d_5$, $k_{190°C} = 2.8$ s$^{-1}$).

After heating a solution of cycloheptatriene **III** in nitrobenzene-$d_5$ for 0.5 h at 130°C, an additional group of signals appeared in the $^1$H NMR spectrum due to isomer **XXI**, the equilibrium **III**-to-**XXI** ratio being 0.59 : 0.41. Isomer **XXI** is formed as a result of 1,5-sigmatropic H-shift from the 7-position to position *3* or *4* in the cycloheptatriene ring (Scheme 9). The energy barriers for the 1,5-H shift in 7-substituted cyclohepta-1,3,5-trienes were determined previously [6]; they range from 30.2 to 33.6 kcal/mol [6].

Thus the calculations showed that cyanocyclopolyenes are considerably more stable than their isocyano isomers. This implies irreversible transformation of isocyanide into cyanide according to the 1,2-shift mechanism for cyclopropene and cyclopentadiene derivatives ($\Delta E^{\neq}$ = 35.0 and 37.5 kcal/mol, respectively) and previously unknown 2,5-sigmatropic shift for isocyanocycloheptatriene. The barrier to the isomerization of the latter in the gas phase ($\Delta E^{\neq}$ = 26.4 kcal/mol) suggests that the transformation of the isocyanide into cyanide is possible to be complete in several hours at room temperature and that the isomerization in strongly polar solvents should occur at a high rate through a ion pair-like transition state ($\Delta E^{\neq}$ = 13.0 kcal/mol, DMSO).

The calculated activation barriers for 1,3-sigmatropic shifts of the cyano group in cyanocyclopropene ($\Delta E^{\neq}$ = 72.2 kcal/mol) are so high that these transformations are impossible under experimental conditions. The cyano and isocyano groups in the cyclopentadiene system are capable of undergoing migration via 1,5-sigmatropic shift in keeping with the Woodward–Hoffman orbital symmetry conservation rules; here, the calculated activation barrier for the CN group migration ($\Delta E^{\neq}$ = 34.4 kcal/mol) approaches the experimental value found for dibenzoindene systems. Both theoretical and experimental data showed that migration of the cyano group in cyanocycloheptatriene follows the 1,5-sigmatropic shift pattern typical of cyclopentadiene derivatives. By contrast, symmetry-forbidden 1,7-shifts of the NC group were revealed at the DFT level for isocyanocycloheptatriene, which may be due to electrostatic interaction between the seven-membered ring and migrating group.

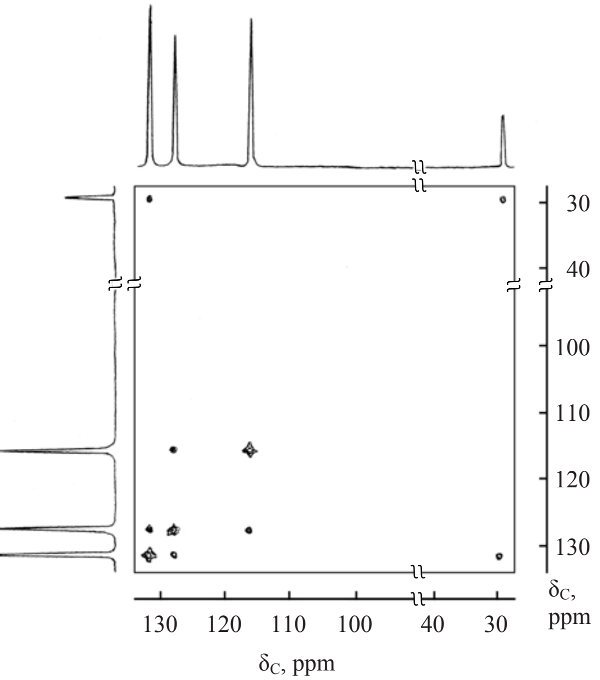


**Fig. 5.** Two-dimensional (EXSY) $^{13}$C NMR spectrum of cyclohepta-2,4,6-triene-1-carbonitrile (**III**) in $C_6D_5NO_2$ at 120°C. Solvent signals are cut off.

## EXPERIMENTAL

Quantum-chemical calculations were performed in the restricted Hartree–Fock (RHF) approximation with account taken of all (valence and inner-shell) electrons in terms of the second-order Møller–Plesset perturbation theory [MP2(full)] [11] and density functional theory (DFT) [11] with three-parameter B3LYP potential and valence-split 6-31G** basis set (Gaussian-03 software package [12]). All stationary points were localized by calculating the Hesse matrix. Topological analysis of total electron density distribution according to Bader (AIM analysis) [33] was performed using AIMPAC software package [34]. The molecular structures shown in Figures 1–4 were plotted using Gauss View 3 program [35].

The $^1$H and $^{13}$C NMR spectra of compound **III** were recorded on Bruker-AM and Varian Unity spectrometers at 300 and 75.47 MHz, respectively, using tetramethylsilane as internal reference. Deuterated solvents were dried over calcined molecular sieves prior to use. The behavior of **III** in solution was studied by dynamic one- and two-dimensional (EXSY) $^{1}$H and $^{13}$C NMR techniques .

Cyclohepta-2,4,6-triene-1-carbonitrile (**III**) was synthesized by reaction of tropylium bromide with potassium cyanide according to the procedure described in [15]. $^{1}$H NMR spectrum (300 MHz, $C_6D_6$), δ, ppm: 2.39 t (1H, 1-H), 4.84 m (2H, 2-H, 7-H), 5.73 m (2H, 3-H, 6-H), 6.23 m (2H, 4-H, 5-H). $^{13}$C NMR spectrum (75.47 MHz, $C_6D_6$), $\delta_C$, ppm: 29.65 ($C^1$), 116.20 ($C^2$, $C^7$), 119.54 (CN), 127.28 ($C^{3,}$ $C^6$), 131.26 ($C^4$, $C^6$).

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 07-03-00223, 06-03-32158a), by the Presidium of the Russian Academy of Sciences (program no. 8, “New Effective Luminophores for Organic Light-Emitting Diodes”), by the Ministry of Education and Science of the Russian Federation (project no. RNP.-2.2.2.2.5592, program for the development of the Southern Federal University), and by the President of the Russian Federation (program for support of leading scientific schools, project no. NSh-363.2008.3).

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