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Structure and Tautomerism of Cyclopentadiene Derivatives: IX.* Synthesis and Structure of Substituted *N*-Cyclopentadienyl Amidinium Ylides**

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Abstract—A procedure has been developed for the synthesis of *N*-cyclopentadienyl amidinium ylides of the general formula $C_5(CO_2Me)_4$[ArNC(Ar′)NHAr]. According to the X-ray diffraction data, ^{1}H and ^{13}C NMR spectroscopy, and MNDO quantum-chemical calculations, the title compounds have a zwitterionic structure with the positive charge localized over the amidine N–C–N triad, and the negative charge, over the cyclopentadiene fragment. The configuration of the amidine moiety is stabilized by additional interaction of the NH hydrogen atom with the negatively charged cyclopentadiene ring (π-bonding). The ylides are chiral due to atropoisomerism arising from a high energy barrier ($\Delta G^{\neq}_{298}$ > 25 kcal/mol) to rotation of the Ar′ substituent about the ordinary C–C bond in the amidinium fragment.

We previously synthesized *N*-pentakis(methoxycarbonyl)cyclopentadienyl amidines which give rise to reversible intramolecular 1,4-sigmatropic shift of methoxycarbonyl group between the cyclopentadiene ring (Cp) and nitrogen atom of the amidine fragment [2]. These compounds were converted into substituted *N*-cyclopentadienyl amidinium ylides which may be regarded as new ligands of the cyclopentadiene series having a donor substituent in the side chain. The synthesis and investigation of N-functionalized cyclopentadienyl ligands and their complexes with metals constitute now a rapidly developing line of the cyclopentadiene chemistry. Such complexes involve metal coordination at the cyclopentadiene fragment and side-chain nitrogen atom. Due to intramolecular coordination, chiral *N*-functionalized cyclopentadienyl ligands give rise to a rigid chiral coordination entity, which makes such complexes attractive for use as catalysts in asymmetric syntheses. Among efficient N-functional groups, substituted aminoethyl and pyridyl side chains must be noted [3–7].

In the preliminary communications [8, 9] we reported on the first examples of chiral cyclopentadienylamidine ligands whose steric structure is suitable for complex formation with metals through both the amidine and the cyclopentadiene fragments. The present article describes the synthesis of *N*,*N′*-diaryl-α-naphth(benz)amidinium-N′-[2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienides], which are new compounds of the cyclopentadiene series having an amidine group in the side chain; their structure in crystal and in solution was examined by X-ray diffraction and ^{1}H and ^{13}C NMR spectroscopy; also, semiempirical quantum-chemical calculations were performed with the goal of elucidating factors stabilizing their zwitterionic structure.

* For communication VIII, see [1].

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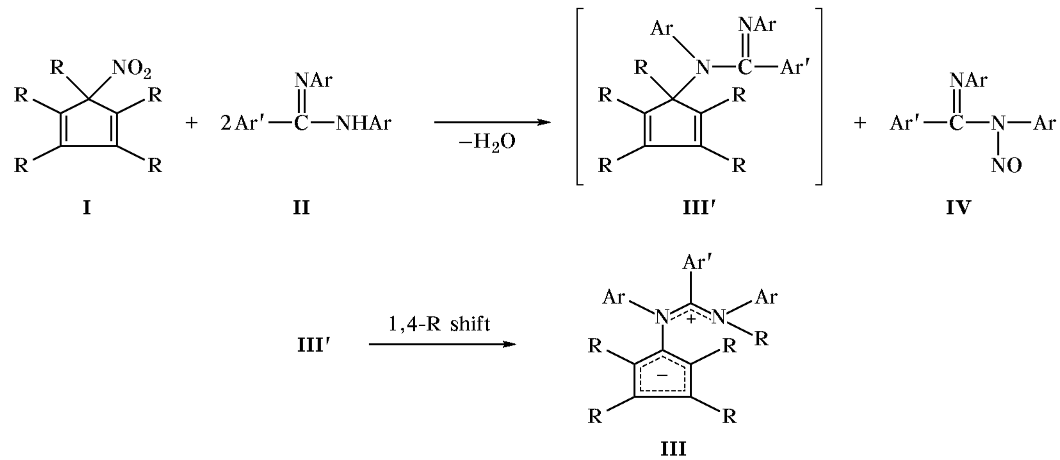
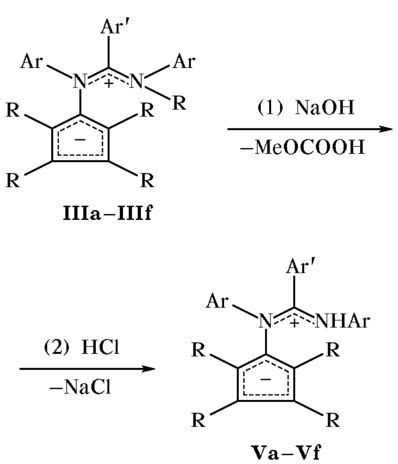
Scheme 1.



R = CO_2Me; Ar = 4(3)-MeC_6H_4; Ar′ = 1-$C_{10}H_7$; 2-XC_6H_4 (X = H, OMe, Cl, Br).

Nucleophilic substitution of the nitro group in 5-nitro-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (**I**) by the amino nitrogen atom of *N*,*N*′-diaryl-α-naphth(benz)amidines **II** is accompanied by 1,4-shift of methoxycarbonyl group in intermediate *N*-cyclopentadienyl amidines **III**′, resulting in formation of *N*-methoxycarbonyl-*N*,*N*′-diaryl-α-naphth-(benz)amidinium-N′-[2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienides] **III** (Scheme 1). Nitrous acid released during the process reacts with excess amidine **II** to give *N*-nitroso derivatives **IV** [10]. Treatment of ylides **III** with sodium hydroxide in methanol leads to elimination of the *N*-methoxycarbonyl group with formation of sodium salts; the latter react with hydrochloric acid to afford *N*,*N*′-diaryl-α-naphth(benz)amidinium-*N*′-[2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienides] **V** in 80–85% yield (Scheme 2).

Scheme 2.



R = CO_2Me, Ar′ = 1-$C_{10}H_7$, Ar = 4-MeC_6H_4 (**a**), 3-MeC_6H_4 (**b**); R = CO_2Me, Ar = 4-MeC_6H_4, Ar′ = Ph (**c**), 2-$MeOC_6H_4$ (**d**), 2-ClC_6H_4 (**e**), 2-BrC_6H_4 (**f**).

The zwitterionic structure of ylide **Va** with hydrogen atom localized on the N^{21} atom was proved by the X-ray diffraction data (Fig. 1). The C–C bond lengths in the cyclopentadiene ring of **Va** range from 1.38 (2) to 1.42 (2) Å, which are typical of substituted cyclopentadienide ions [11]. The N^6–C^{14} and N^{21}–C^{14} bonds in the amidine fragment have very similar lengths, 1.25 (2) and 1.32 (2) Å, in keeping with published data for amidinium ions [2]. Structure **Va** is characterized by *E*-configuration of the amidine fragment with respect to the C^{14}–N^{21} bond; this means that the hydrogen atom is located at the same side of this bond as the N′CpAr moiety. In addition, short distances between the hydrogen atom on N^{21} and carbon atoms of the cyclopentadiene ring (C^1–C^5) should be noted: 1.87 (3), 2.56 (3), 3.31 (3), 3.28 (3), and 2.46 (3) Å, respectively. The plane of the amidine fragment is almost orthogonal to the cyclopentadiene ring plane: the torsion angle $C^{14}N^6C^1C^5$ is –93.3° (Fig. 1). The above short distances suggest formation of hydrogen bond with the π-system of the cyclopentadiene ring.

Molecule **Va** is sterically overcrowded: two methoxycarbonyl groups are considerably turned apart relative to the cyclopentadiene ring plane (Fig. 1). The angles at the sp^2-hybridized amidine carbon atom are distorted because of steric hindrance: $N^6C^{14}N^{21}$ 112 (2), $N^6C^{14}C^{15}$ 114(2), $N^{21}C^{14}C^{15}$ 129 (2)°. Both *p*-tolyl substituents in the amidine fragment deviate from the amidine group plane: the torsion angles

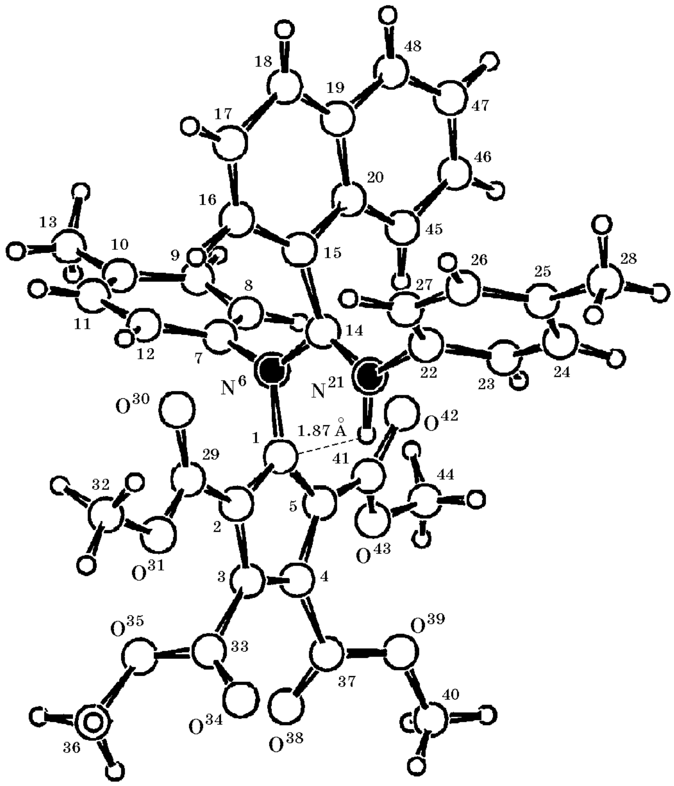


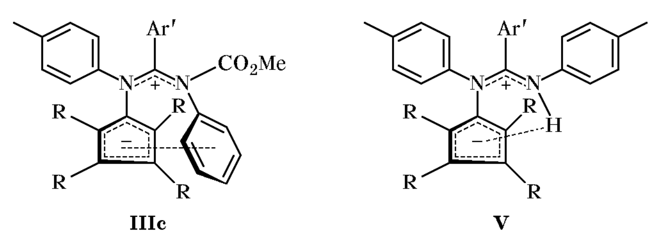
Fig. 1. Structure of the molecule of compound **Va** according to the X-ray diffraction data. Selected bond lengths, Å: C^1-C^2 1.38 (2), C^2-C^3 1.39 (2), C^3-C^4 1.41 (2), C^4-C^5 1.42 (2), C^1-C^5 1.42 (2), N^6-C^{14} 1.25 (2), $N^{21}-C^{14}$ 1.32 (2), N^6-C^1 1.50 (2). Selected bond angles, deg: $C^1C^2C^3$ 111.1 (13), $C^2C^3C^4$ 105.9 (12), $C^3C^4C^5$ 109.1 (13), $C^4C^5C^1$ 106.1 (14), $C^2C^1C^5$ 107.6 (12), $N^6C^{14}N^{21}$ 112 (2), $C^{14}N^6C^1$ 115 (2), $N^6C^{14}C^{15}$ 114 (2), $N^{21}C^{14}C^{15}$ 129 (2), $C^2C^1N^6$ 124.8 (14), $C^5C^1N^6$ 125.9 (14). Selected torsion angles, deg: $C^1C^2C^{29}O^{30}$ 5 (3), $C^2C^3C^{33}O^{35}$ 66 (2), $C^3C^4C^{37}O^{39}$ 127.2 (16), $C^1C^5C^{41}O^{42}$ 21 (3).

$C^{14}N^6C^7C^8$ and $C^{14}N^{21}C^{22}C^{23}$ are equal to 72 (3) and –118 (3)°, respectively. Despite such a conformation of the *N*-*p*-tolyl fragments, the bulky naphthyl group is not coplanar to the amidine fragment, and the corresponding torsion angle $N^6C^{14}C^{15}C^{16}$ is 63 (4)°. As a result, the molecule of ylide **Va** is chiral.

Figure 2 shows the structure of ylide **Vc**; its structural parameters were reported by us previously [8]. Unlike compound **Va**, the phenyl group at C^{14} in molecule **Vc** lies in the plane of the amidine fragment; in addition, it has a symmetry axis so that molecule **Vc** is characterized by a C_s symmetry.

In contrast to ylides **Va** and **Vc**, their precursor, pentakis(methoxycarbonyl)cyclopentadiene exists in the hydroxyfulvene form where the hydrogen atom is located between the carbonyl oxygen atoms of vicinal methoxycarbonyl groups [11]. According to the X-ray diffraction data [2], structurally related ylide **IIIc** has *E* configuration with the tolyl and N′CpAr fragments located at one side of the C=N bond; π-interaction between the *N*-aryl and cyclopentadiene rings gives rise to charge-transfer band at λ 475 nm (ε = 10 400) in the UV spectrum (Scheme 3).

Scheme 3.



R = CO_2Me.

By contrast, *E* configuration of ylides **V** (where the hydrogen atom and the N′CpAr fragment are arranged at one side relative to the C=N bond) lacks π-interaction between the aryl and cyclopentadiene rings, and UV absorption bands of compounds **V** are displaced toward shorter wavelengths (CH_3OH): **Vb**, λ_{max} 260 nm (ε = 30 200), 290 nm (ε = 16 000).

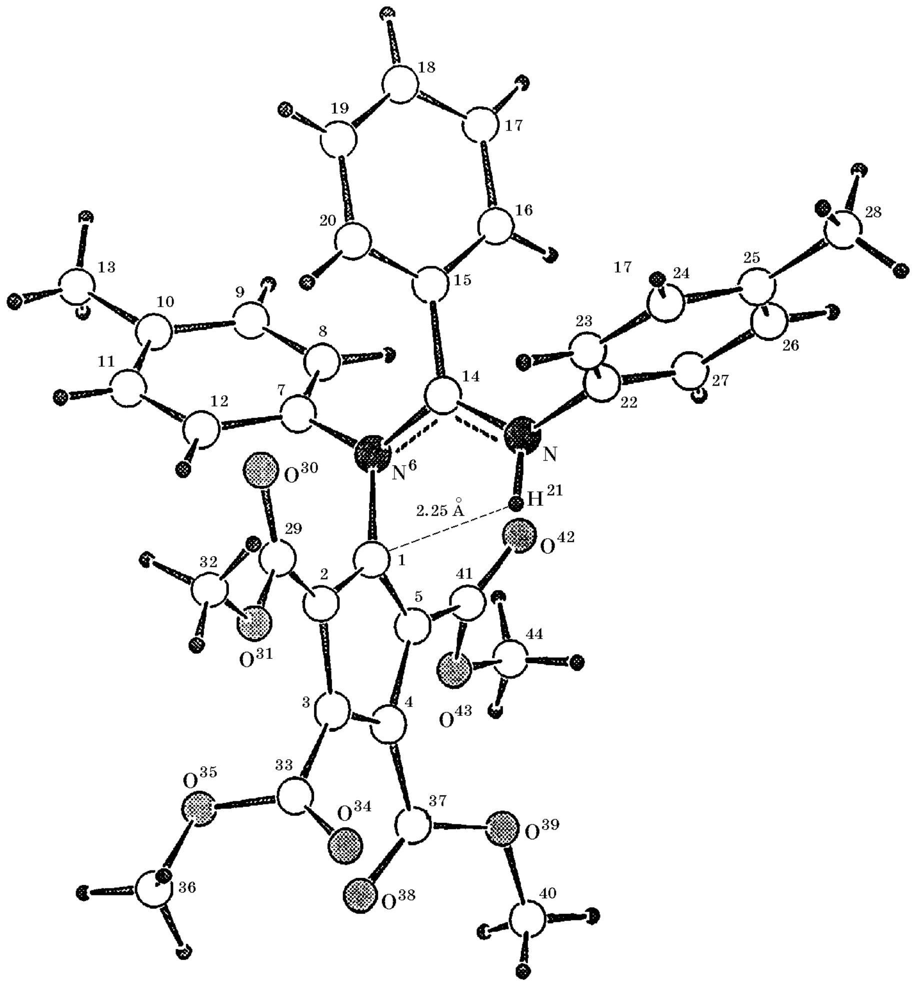


Fig. 2. Structure of the molecule of compound **Vc** according to the X-ray diffraction data. Selected bond lengths, Å: C^1-C^2 1.40 (1), C^2-C^3 1.42 (1), C^3-C^4 1.38 (1), C^4-C^5 1.42 (1), C^1-C^5 1.37 (1), N^6-C^{14} 1.31 (1), $N^{21}-C^{14}$ 1.31 (1), N^6-C^1 1.45 (1); selected angles, deg: $N^6C^{14}N^{21}$ 119.8 (8), $C^{14}N^6C^1$ 121.5 (7), $N^6C^{14}C^{15}$ 119.6 (7), $N^{21}C^{14}C^{15}$ 120.5 (8).

Table 1. Melting points, elemental analyses, and IR and ^{1}H NMR (300 MHz) spectra of compounds **IIIa–IIIf** and **Va–Vf**

Compound no.	mp, °C	Found, %			Formula	Calculated, %		
		C	H	N		C	H	N
IIIa	139–140	68.09	5.22	3.89	$C_{40}H_{36}N_2O_{10}$	68.17	5.16	3.80
IIIb	105–106	68.08	5.11	3.74	$C_{40}H_{36}N_2O_{10}$	68.17	5.16	3.80
IIIc	161–162	66.00	5.18	4.35	$C_{36}H_{34}N_2O_{10}$	66.05	5.23	4.28
IIId	176–177	64.84	5.39	4.11	$C_{37}H_{36}N_2O_{11}$	64.91	5.30	4.09
IIIe	118–119	62.67	4.73	3.99	$C_{36}H_{33}ClN_2O_{10}$[a]	62.74	4.82	4.06
IIIf	121–122	58.89	4.46	3.90	$C_{36}H_{33}BrN_2O_{10}$[b]	58.94	4.53	3.82
Va	254–255	70.51	5.22	4.25	$C_{38}H_{34}N_2O_8$	70.58	5.30	4.33
Vb	244–245	70.53	5.35	4.27	$C_{38}H_{34}N_2O_8$	70.58	5.30	4.33
Vc	252–253	68.39	5.45	4.64	$C_{34}H_{32}N_2O_8$	68.43	5.41	4.70
Vd	248–249	67.04	5.39	4.51	$C_{35}H_{34}N_2O_9$	67.08	5.47	4.47
Ve	258–259	64.62	5.01	4.50	$C_{34}H_{31}ClN_2O_8$[c]	64.71	4.95	4.43
Vf	248–249	60.39	4.70	4.06	$C_{34}H_{31}BrN_2O_8$[d]	60.45	4.63	4.15

Table 1. (Contd.)

Compound no.	IR spectrum,[e] ν, cm^{-1}	^1H NMR spectrum ($CDCl_3$, 298 K), δ, ppm			
		Me, s	OMe, s	Ar, m	NH, s
IIIa	1775, 1740, 1700, 1680, 1510, 1265, 1200, 1160, 1090	2.01 (3H), 2.14 (3H)	3.45 (3H), 3.53 (3H), 3.72 (3H), 3.73 (3H), 3.76 (3H)	6.61–8.42 (15H)	
IIIb	1770, 1730, 1705, 1690, 1670, 1270, 1210, 1170, 1090	2.01 (3H), 2.14 (3H)	3.51 (3H), 3.54 (3H), 3.71 (3H), 3.73 (3H), 3.75 (3H)	6.76–8.44 (15H)	
IIIc	1780, 1735, 1730, 1700, 1695, 1500, 1280, 1220, 1210, 1180, 1100, 1075	2.21 (3H), 2.32 (3H)	3.49 (3H), 3.51 (6H), 3.71 (6H)	6.90–7.67 (13H)	
IIId	1775, 1740, 1730, 1700, 1695, 1510, 1290, 1285, 1215	2.19 (3H), 2.28 (3H)	3.41 (3H), 3.55 (3H), 3.67 (3H), 3.75 (3H), 3.80 (3H), 3.85 (3H)	6.87–7.69 (12H)	
IIIe	1770, 1735, 1710, 1680, 1665, 1280, 1250, 1205, 1170	2.14 (3H), 2.27 (3H)	3.33 (3H), 3.56 (3H), 3.68 (3H), 3.74 (3H), 3.79 (3H)	6.63–7.85 (12H)	
IIIf	1765, 1725, 1700, 1690, 1665, 1270, 1245, 1200, 1160	2.12 (3H), 2.27 (3H)	3.31 (3H), 3.57 (3H), 3.69 (3H), 3.74 (3H), 3.78 (3H)	6.67–7.75 (12H)	
Va	3265, 1750, 1725, 1705, 1680, 1600, 1580, 1290, 1200	1.98 (3H), 1.99 (3H)	3.71 (3H), 3.75 (3H), 3.80 (3H), 3.81 (3H)	6.59–8.29 (15H)	8.70 (1H)
Vb	3260, 1740, 1720, 1700, 1680, 1610, 1570, 1290, 1220, 1180	1.98 (3H), 2.02 (3H)	3.77 (3H), 3.81 (3H), 3.86 (3H), 3.87 (3H)	6.65–8.32 (15H)	8.86 (1H)
Vc	3280, 1740, 1705, 1700, 1675, 1620, 1610, 1580, 1280, 1230, 1190, 1075	2.10 (3H), 2.17 (3H)	3.69 (6H), 3.76 (6H)	6.76–7.39 (13H)	8.52 (1H)
Vd	3275, 1735, 1710, 1700, 1680, 1620, 1600, 1580, 1270, 1230, 1200, 1090	2.11 (3H), 2.19 (3H)	3.69 (3H), 3.74 (3H), 3.82 (3H), 3.83 (3H), 3.85 (3H)	6.79–7.45 (12H)	8.60 (1H)
Ve	3290, 1740, 1710, 1705, 1680, 1630, 1600, 1590, 1290	2.13 (3H), 2.20 (3H)	3.70 (3H), 3.76 (3H), 3.80 (3H), 3.81 (3H)	6.81–7.88 (12H)	8.58 (1H)
Vf	3280, 1725, 1705, 1685, 1665, 1610, 1590, 1570, 1270	2.12 (3H), 2.20 (3H)	3.69 (3H), 3.76 (3H), 3.79 (3H), 3.81 (3H)	6.81–7.96 (12H)	8.62 (1H)

[a] Found Cl, %: 5.09; calculated Cl, %: 5.14.
[b] Found Br, %: 10.80; calculated Br, %: 10.89.
[c] Found Cl, %: 5.68; calculated Cl, %: 5.61.
[d] Found Br, %: 11.90; calculated Br, %: 11.83.
[e] In mineral oil.

The data of X-ray analysis (Figs. 1, 2), IR and ^1H and ^{13}C NMR spectroscopy (Tables 1, 2), and mass spectrometry indicate that compounds **Va**–**Vf**, as well as their precursors **IIIa**–**IIIf**, have zwitterionic structure both in the solid state and in solution. The IR spectra of **III** and **V** lack C=N and $C=C_{Cp}$ absorption, but four carbonyl bands are observed since the methoxycarbonyl groups are forced out from the cyclopentadiene ring at different angles (Fig. 1) and are nonequivalent. The presence in the mass spectra of compounds **Va**–**Vf** of the $[M-NHC_6H_4Me]^+$, $[M-ArCNHC_6H_4Me]^+$, and $[ArCNHC_6H_4Me]^+$ ion peaks also indicates delocalization of the π-C=N bond over the N–C–N amidine triad.

In the ^{13}C NMR spectra of **III** and **V** all signals from carbon atoms of the cyclopentadiene ring appear in the range from δ_C 105 to 124 ppm, indicating the absence of sp^3-hybridized carbon atom. The upfield shift of the signals relative to those observed in the spectrum of 5-methyl-1,2,3,4,5-pentakis(methoxycar-

Table 2. ^{13}C NMR spectra[a] (75.47 MHz, δ_C, ppm) of compounds **IIIa–IIId**, **IIIf**, **Va–Vc**, **Vf**, and **VI** at 298 K

Comp. no.	R[a]	Solvent	C=O	NCN	C_{arom}	C^1 (Cp)	C^2–C^5 (Cp)	OCH_3	CH_3
IIIa	CO_2Me	CD_3CN (342 K)	164.92, 166.19, 167.84, 167.94, 168.00	153.55	124.84, 125.55, 125.79,[c] 126.86, 127.61, 127.94, 128.31,[c] 129.19, 129.44, 129.80, 129.92, 131.50,[c] 133.49,[c] 133.92, 135.94, 139.57,[c] 140.27,[c] 142.39[c]	120.30	108.79, 111.08, 119.19	50.90, 51.31, 51.50, 51.54, 56.43	20.69, 20.88
IIIb	CO_2Me	CD_2Cl_2	164.20, 165.37, 167.49, 167.50, 167.51	152.95	123.91, 124.93, 125. 32,[c] 126.77, 127.25, 127.64, 127.78,[c] 128.27, 128.87, 129.30, 130.88,[c] 133.08, 133.46,[c] 137.39, 138.51,[c] 139.36,[c] 143.56[c]	120.01	107.11, 110.92, 118.20	50.85, 51.31, 51.61, 51.65, 56.23	20.98, 20.99
IIIc	CO_2Me	$CDCl_3$	163.99, 167.30, 168.14	153.29	126.26, 127.32, 128.39, 128.88, 129.38, 130.86, 131.62,[c] 132.73, 133.29,[c] 138.43,[c] 139.56,[c] 139.88[c]	124.89	108.69, 118.82	50.54, 51.33, 54.92	20.89, 21.01
IIId	CO_2Me	$CDCl_3$	158.07, 162.67, 166.08, 166.59, 168.48	153.33	121.17, 125.18,[c] 127.63, 128.33, 128.88, 129.51, 133.93, 134.10,[c] 134.24, 135.72,[c] 138.39,[c] 139.35,[c] 140.55[c]	120.02	106.57, 110.74, 114.25	50.06, 51.31, 51.39, 51.54, 54.85, 55.88	20.99, 21.11
IIIf	CO_2Me	$CDCl_3$	162.26, 166.09, 166.10, 166.71, 168.51	152.77	122.19,[c] 125.27, 127.61, 128.66, 129.33, 132.17,[c] 133.06, 133.40, 135.60,[c] 138.90,[c] 139.96,[c] 140.50[c]	124.61	106.94, 112.58, 113.24, 124.14	49.99, 51.27, 51.56, 51.67, 55.35	20.96, 21.12
Va	H	$CDCl_3$	165.36, 165.37, 167.07, 168.35	165.72	124.16,[c] 124.39, 124.59, 125.35, 125.39, 126.72, 128.08, 128.47, 128.99, 129.24, 129.89,[c] 130.38, 131.95, 132.26,[c] 132.49,[c] 137.61,[c] 137.66,[c] 139.21[c]	123.12	105.76, 110.37, 117.70, 120.31	51.21, 51.22, 51.54, 51.82	20.74, 20.75
Vb	H	$CDCl_3$	165.50, 165.63, 167.05, 168.40	165.86	122.52, 122.83, 122.91, 124.59, 126.04, 126.29, 126.80, 128.04, 128.07, 128.43, 128.49, 128.69, 130.05,[c] 130.46, 132.09, 132.61,[c] 134.91,[c] 138.55,[c] 138.83,[c] 141.67[c]	124.33	106.00, 110.67, 117.55, 120.50	51.24, 51.30, 51.57, 51.85	20.88, 21.06
Vc	H	$CDCl_3$	165.23, 167.70	165.76	125.84, 126.50, 126.64,[c] 128.53, 129.03, 129.75, 130.77, 131.67, 132.91,[c] 137.30,[c] 137.69,[c]138.99[c]	123.90	107.96, 118.86	51.15, 51.67	20.86, 20.90
Vf	H	$CDCl_3$	164.77, 165.38, 166.97, 168.45	164.20	121.89,[c] 125.62, 125.90, 127.60, 128.75,[c] 129.23, 129.41, 131.81,[c] 132.70, 133.88, 133.34, 138.00,[c] 138.10,[c] 138.83[c]	122.60	104.70, 111.25, 117.81, 120.59	51.18, 51.19, 51.57, 51.87	20.92, 21.01

Table 2. (Contd.)

Comp. no.	R[a]	Solvent	C=O	NCN	C_{arom}	C^1 (Cp)	C^2–C^5 (Cp)	OCH_3	CH_3
VI	Na	C_6D_6[d]	166.49, 166.50, 169.84, 170.15	159.48	123.01, 124.85, 125.66, 126.22, 127.00, 129.53, 129.98, 131.83,[c] 132.81,[c] 133.25,[c] 133.68,[c] 137.90,[c] 143.84,[c] 148.90[c]	118.42	110.07, 111.61, 117.24	50.44, 51.34	20.39, 20.51

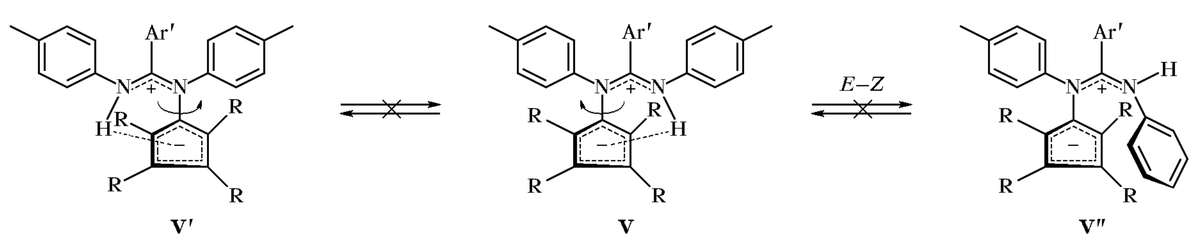
[a] Substituent on the nitrogen atom.
[b] Signals were assigned using the APT (Approach Proton Test) sequence.
[c] *ipso*-Carbon atom.
[d] In the presence of 1 equiv of crown-5.

bonyl)cyclopentadiene [12] (δ_C 140.62, 145.46 ppm) is explained by delocalization of the negative charge over the cyclopentadiene ring. The amidine moiety gives rise to a signal at δ_C 152–165 ppm, i.e., in the region typical of positively charged carbon atoms. These data are consistent with the ylide structure of compounds **III** and **V**.

A considerable difference between the chemical shifts of the amidine carbon atoms in NH-derivatives **V** (δ_C 164–165 ppm) and ylides **III** (δ_C 152–153 ppm, Table 2) results from additional coordination of the NH hydrogen atom to the π system of the cyclopentadiene ring. Such coordination also induces a downfield shift of the C^1 signal in **V** (δ_C 123–124 ppm) relative to analogous signal of sodium 1-[*N*,*N'*-di-*p*-tolyl-α-naphthylamidino]-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienide (**VI**). In the presence of crown-5 (in (C_6D_6), the corresponding signal appears at δ_C 118.42 ppm (Table 2). An analogous criterion was used in [4–7] to prove π-coordination of metals to cyclopentadiene ring. The zwitterionic structure of **V** is retained in both polar and nonpolar solvents. This structure is characterized by orthogonal arrangement of the amidine fragment (possessing bulky substituents) and cyclopentadiene ring, which gives rise to π-coordination of hydrogen and hampers rotation about the C_{Cp}–N bond in solution. Likewise, restricted rotation of bulky *ortho*-substituted aryl groups about the C–C bond in 2-aryl-1,3,4,5,5-pentakis(methoxycarbonyl)cyclopentadienes was observed by us previously; according to the ^1H NMR data [13], it is characterized by a fairly high energy barrier ($\Delta G^{\neq}_{298}$ = 21.3 kcal/mol, Ar = $C_6H_4NO_2$-2).

The ^1H NMR spectra of compounds **IIIc** and **Vc** which possess a phenyl group at the amidine carbon atom (C_s symmetry) contain two six-proton signals from the methoxycarbonyl groups (Fig. 3, Table 1). Correspondingly, the ^{13}C NMR spectra of these compounds contain signals from equivalent in pairs carbon atoms of both carbonyl and methoxy groups, as well as of the C^2, C^5 and C^3, C^4 atoms of the cyclopentadiene ring (Fig. 4, Table 2). By contrast, protons of the methoxycarbonyl groups (in the ^1H NMR spectra) and carbon nuclei of both carbonyl and methoxy groups (^{13}C NMR) of ylides **IIIa**, **IIIb**, **IIId**–**IIIf**, **Va**, **Vb**, and **Vd**–**Vf** (which possess axially asymmetric α-naphthyl or *ortho*-substituted phenyl group at the amidine carbon atom) are magnetically nonequivalent, and they give rise to four separate signals in each particular case. Likewise, the cyclopentadiene carbon atoms (C^2–C^5) are also represented in the ^{13}C NMR spectrum by four different signals (Fig. 4, Table 2). These findings indicate the lack of C_s symmetry in molecules **III** and **V** having an α-naphthyl or *ortho*-substituted phenyl group; therefore, such molecules are chiral.

Scheme 4.



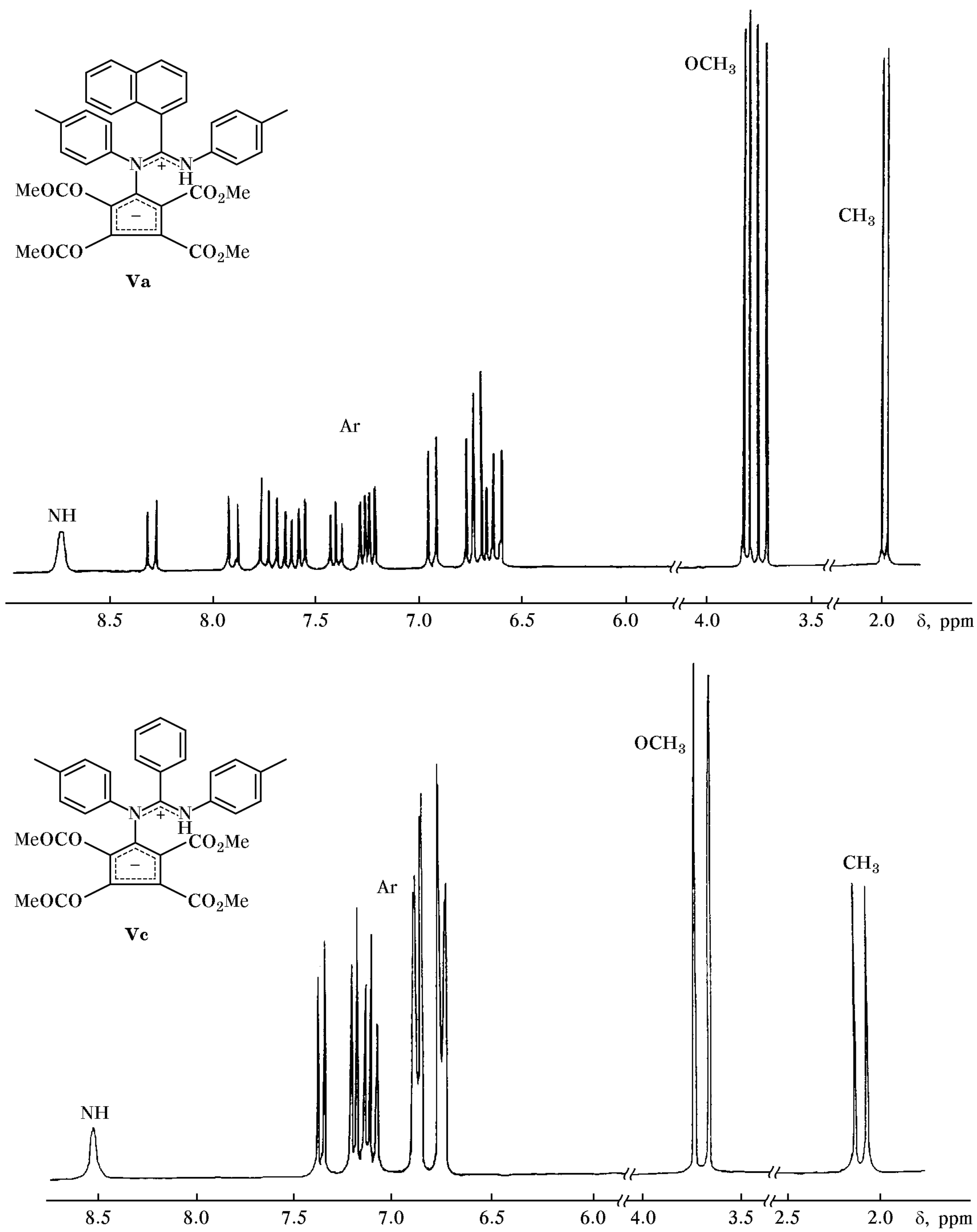


Fig. 3. ^{1}H NMR spectra (300 MHz) of compounds **Va** and **Vc** in $CDCl_3$ at 22°C.

No changes in the NMR spectra were observed on heating of solutions of compounds **Va**, **Vb**, and **Vd**–**Vf** in nitrobenzene-d_5 to 180°C or in toluene-d_8 to 110°C [in the latter case, even in the presence of "proton sponge," 1,8-bis(dimethylamino)naphthalene]. Hence the chiral structure of these compounds is stable. This property is important, for introduction of rigid methylene bridges is necessary for most compounds whose chirality originates from restricted rotation of bulky substituents to fix their enantiomeric conformation [14]. Although compounds **Va**, **Vb**, and **Vd**–**Vf** were isolated as racemic mixtures, the stability of their chiral structure suggests that the racemic mixtures could be separated into individual enantiomers.

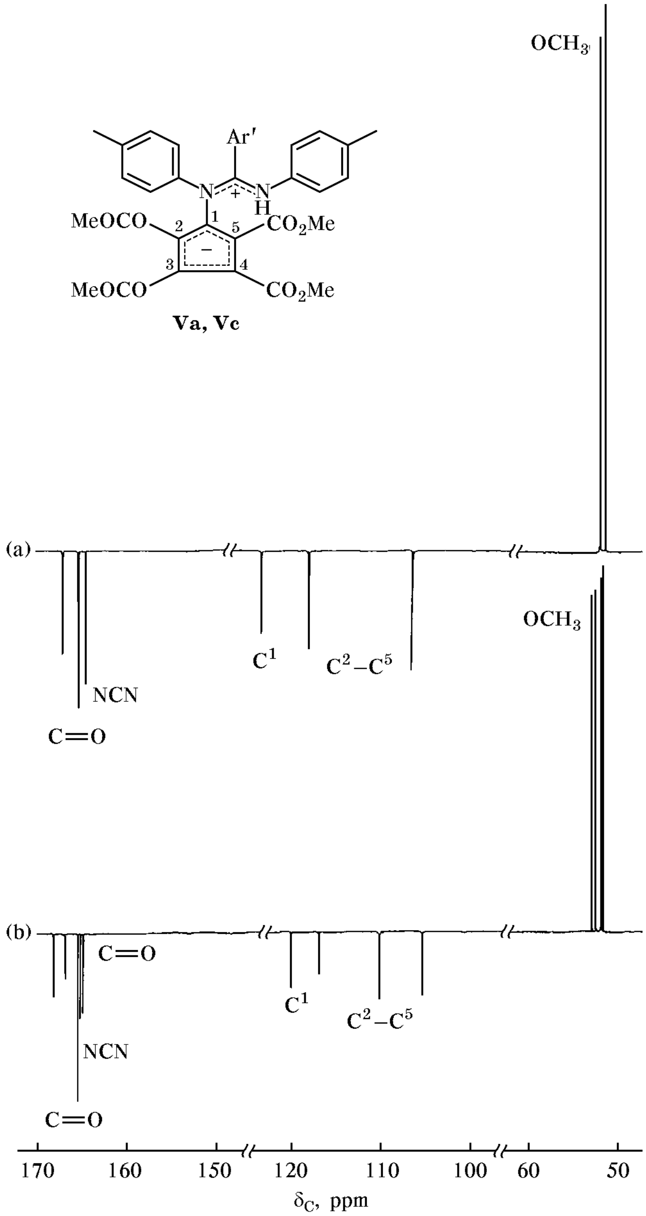
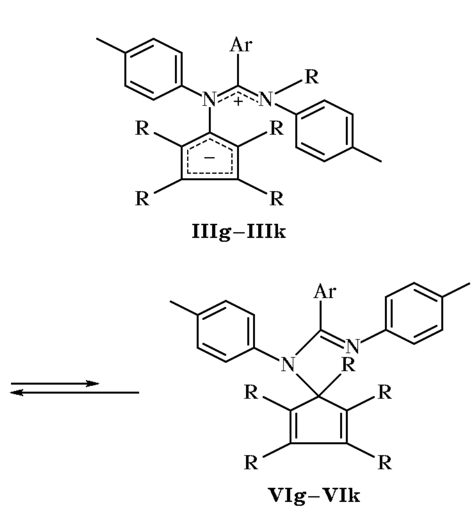


Fig. 4. ^{13}C NMR spectra (75.47 MHz, $CDCl_3$, APT) of ylides **Va** and **Vc** in the regions corresponding to carbonyl carbon atoms, cyclopentadiene ring, and methoxy groups.

As follows from the NMR data, the chirality of naphth(benz)amidiniocyclopentadienides **Va**, **Vb**, and **Vd**–**Vf** arises from atropoisomerism. The stability of chiral structures is likely to be determined by high energy barrier to rotation of the α-naphthyl or *ortho*-substituted phenyl group ($\Delta G^{\neq}_{298}$ > 25 kcal/mol) about the C–C bond and also by stabilization of *Z,E*-configuration of the amidine fragment in the above conformation of molecules **V** due to π-H-bonding. Such π-bond hampers free rotation of the amidine moiety about the C_{Cp}–N bond and *E*–*Z*-isomerization about the C=N bond (Scheme 4). Moreover, it is known [15] that the barrier to *E*–*Z*-isomerization in amidinium ions is sufficiently high. Atropoisomeric chiral amidinium ions having biaryl fragments were recently proposed as new structures for "host–guest" complex formation [14].

We previously revealed a reversible intramolecular 1,4-shift of methoxycarbonyl group between nitrogen atom of the amidine triad and cyclopentadiene ring in ylides **IIIg**–**IIIk** ($\Delta G^{\neq}_{353}$ = 27.6–28.8 kcal/mol, Scheme 5) [2].

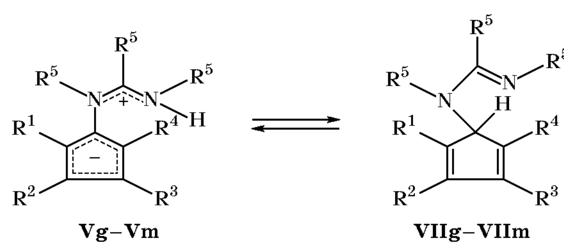
Scheme 5.



R = CO_2Me; Ar = 4-XC_6H_4: X = NO_2 (**g**), Br (**h**), H (**i**), Me (**j**), OMe (**k**).

An analogous process could be expected for ylides **V** (Scheme 6) via reversible proton transfer leading to cyclopentadienylamidines **VII**.

Scheme 6.



$R^1 = R^2 = R^3 = R^4 = R^5$ = H (**g**); $R^1 = R^2 = R^3 = R^4$ = H, R^5 = Ph (**h**); R^1 = CO_2Me, $R^2 = R^3 = R^4 = R^5$ = H (**i**); $R^1 = R^2$ = CO_2Me, $R^3 = R^4 = R^5$ = H (**j**); $R^1 = R^2 = R^3$ = CO_2Me, $R^4 = R^5$ = H (**k**); $R^1 = R^2 = R^3 = R^4$ = CO_2Me, R^5 = H (**l**); $R^1 = R^2 = R^3 = R^4$ = CO_2Me, R^5 = Ph (**m**).

Table 3. Relative energies of isomers **Vg–Vm** and **VIIg–VIIm** and energy barriers to the rearrangement **V**⇄**VII** according to the results of MNDO calculations, kcal/mol

Comp. no.	Substituent					E(**V**)	E(**VII**)	E(**V** → **VII**)	E(**VII** → **V**)
	R^1	R^2	R^3	R^4	R^5				
Vg, **VIIg**	H	H	H	H	H	17.2	0	31.2	48.4
Vh, **VIIh**	H	H	H	H	Ph	24.7	0	17.4	42.1
Vi, **VIIi**	CO_2Me	H	H	H	H	11.8	0	33.2	45.0
Vj, **VIIj**	CO_2Me	CO_2Me	H	H	H	6.8	0	36.5	43.3
Vk, **VIIk**	CO_2Me	CO_2Me	CO_2Me	H	H	1.9	0	38.7	40.6
Vl, **VIIl**	CO_2Me	CO_2Me	CO_2Me	CO_2Me	H	0	4.7	44.0	39.3
Vm, **VIIm**	CO_2Me	CO_2Me	CO_2Me	CO_2Me	Ph	0	3.8	35.7	31.9

However, we failed to detect compounds **VII** experimentally. A possible reason is either a lower energy of compounds **V** relative to isomers **VII** or a high energy barrier (≥35 kcal/mol) to the rearrangement shown in Scheme 6, or both these. To verify this assumption, we performed MNDO quantum-chemical calculations of the total energy of compounds **Vg**–**Vm** and **VIIg**–**VIIm** (which are structurally related to structures **Va**–**Vf**) in the ground state and also estimated energy barriers to the isomerization **V**⇄**VII**. According to the calculations, structure **VIIg** is by 17.2 kcal/mol more stable than its isomer **Vg** (Table 3); likewise, the energy difference for compounds **Vh** and **VIIh** is ΔE = 24.7 kcal/mol. Successive replacement of hydrogen in the cyclopentadiene ring by methoxycarbonyl groups leads to leveling of the energies of structures **V** and **VII** (Table 3); when all hydrogen atoms are replaced by methoxycarbonyl groups, the energies of the ground states of molecules **V** and **VII** are arranged in the reversed order, i.e., ylides **Vl** ($R^1 = R^2 = R^3 = R^4 = CO_2Me$, R^5 = H) and **Vm** ($R^1 = R^2 = R^3 = R^4 = CO_2Me$, R^5 = Ph) become more energetically favorable than their isomers **VIIl** and **VIIm** by 4.7 and 3.8 kcal/mol, respectively. The same order is observed for variation of the energy barrier to the transformation **VII** → **V**: from 48.4 to 31.9 kcal/mol; simultaneously, ΔE(**V** → **VII**) increases from 17.4 to 44.0 kcal/mol (Table 3). Although compound **Vm**, which is most related to ylides **Va**–**Vf**, is only slightly (by 3.8 kcal/mol) more stable than its isomer **VIIm**, it is difficult to detect the latter experimentally because of relatively high (35.7 kcal/mol, Table 3) energy barrier to its formation from ylide **Vm** via proton transfer from nitrogen atom of the amidine triad to the cyclopentadiene ring.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AM instrument at 300 MHz from 0.05 M solutions. The ^{13}C NMR spectra (including those obtained using the APT sequence) were measured on a Bruker AM spectrometer at 75.47 MHz from 0.5 M solutions. The IR spectra were obtained on a Specord IR75 instrument from samples dispersed in mineral oil. The mass spectra (70 eV) were run on an HP 5995A mass spectrometer with direct sample admission into the ion source (60°C).

X-Ray diffraction study of compound Va. $C_{38}H_{34}N_2O_8 \cdot 1/2C_6H_6$. M 685.73. Monoclinic crystals, space group $C2/c$; unit cell parameters: a = 29.814(10), b = 15.108(10), c = 19.998(10) Å; β = 127.21(3)°, V = 7174(6) Å^3; Z = 8; d_{calc} = 1.270 g/cm^3. The data were acquired using an Enraf–Nonius CAD-4 diffractometer, T = 293(2) K, Mo$K\alpha$ irradiation, λ = 0.71070 Å, $\theta/2\theta$-scanning. The structure was solved by the direct method using SHEXS-97 program. Absorption coefficient 0.089 mm^{-1}, $F(000)$ = 2888; scan range θ 1.60–19.99°; spherical segment $0 \le h \le 28$, $0 \le k \le 14$, $-19 \le l \le 15$. The number of measured reflections was 3325/3317, 3336 of which were independent [R(int) = 0.0621]. Least-squares procedure gave GOF = 1.442 with respect to F^2; the final divergence factors were [$I > 2\sigma(I)$]: R_1 = 0.1440, wR_2 = 0.2912; all data: R_1 = 0.2812, wR_2 = 0.3455, Δf_{max} = 0.640 e Å^{-3}. Hydrogen atoms were localized from geometric considerations, and their positions were refined using the “rider” model. The coordinates of non-hydrogen atoms and their equivalent thermal parameters are given in Table 4.

Quantum-chemical calculations were performed by the MNDO semiempirical procedure using Hyper-

Table 4. Coordinates of non-hydrogen atoms ($\times 10^4$) and their equivalent temperature factors[a] ($U_{eq} \times 10^3$) in structure **Va**

Atom	*x*	*y*	*z*	U_{eq}/Å^2	Atom	*x*	*y*	*z*	U_{eq}/Å^2
O^{30}	–2899 (4)	–334 (7)	–3757 (6)	103 (4)	C^{16}	–1438 (8)	–453 (17)	–2535 (11)	155 (11)
O^{31}	–3804 (4)	–196 (9)	–4350 (7)	123 (5)	C^{17}	–975 (11)	–180 (13)	–2457 (13)	185 (11)
O^{34}	–4634 (4)	–671 (8)	–3816 (6)	103 (4)	C^{18}	–418 (8)	–350 (15)	–1665 (13)	170 (12)
O^{35}	–4560 (4)	–1547 (7)	–4583 (7)	86 (4)	C^{19}	–425 (6)	–824 (13)	–1065 (12)	96 (7)
O^{38}	–4415 (5)	–2556 (9)	–2896 (7)	121 (5)	C^{20}	–925 (8)	–969 (15)	–1138 (13)	227 (19)
O^{39}	–3751 (4)	–2136 (7)	–1578 (6)	90 (4)	C^{22}	–1828 (9)	328 (16)	–1060 (17)	174 (14)
O^{42}	–2090 (4)	–2364 (7)	–810 (6)	87 (4)	C^{23}	–1701 (11)	382 (17)	–266 (18)	151 (13)
O^{43}	–2837 (4)	–3190 (8)	–1233 (6)	100 (4)	C^{24}	–1509 (11)	1160 (2)	178 (14)	202 (17)
N^{6}	–2253 (6)	–1533 (12)	–2321 (11)	104 (5)	C^{25}	–1365 (9)	1875 (17)	–105 (16)	151 (14)
N^{21}	–2124 (7)	–434 (17)	–1560 (15)	184 (13)	C^{26}	–1497 (12)	1815 (18)	–899 (18)	197 (15)
C^{1}	–2814 (6)	–1506 (14)	–2487 (11)	121 (8)	C^{27}	–1723 (10)	1050 (18)	–1374 (14)	142 (12)
C^{2}	–3297 (7)	–1153 (12)	–3196 (10)	94 (6)	C^{28}	–1164 (14)	2810 (2)	360 (2)	250 (18)
C^{3}	–3766 (6)	–1374 (10)	–3242 (9)	71 (5)	C^{29}	–3315 (7)	–555 (13)	–3785 (11)	99 (6)
C^{4}	–3570 (5)	–1941 (11)	–2557 (9)	79 (5)	C^{32}	–3866 (6)	394 (13)	–4987 (9)	127 (8)
C^{5}	–2974 (6)	–2015 (12)	–2068 (11)	99 (6)	C^{33}	–4364 (7)	–1173 (12)	–3906 (10)	68 (5)
C^{7}	–2104 (7)	–2273 (13)	–2619 (12)	74 (5)	C^{36}	–5144 (6)	–1369 (11)	–5317 (8)	101 (6)
C^{8}	–1792 (13)	–2993 (19)	–2085 (13)	184 (14)	C^{37}	–3957 (6)	–2289 (12)	–2356 (11)	72 (5)
C^{9}	–1621 (10)	–3666 (17)	–2356 (12)	187 (18)	C^{40}	–4095 (7)	–2492 (13)	–1344 (9)	119 (7)
C^{10}	–1826 (11)	–3729 (16)	–3195 (16)	300 (3)	C^{41}	–2603 (7)	–2481 (11)	–1335 (10)	60 (4)
C^{11}	–2113 (7)	–2996 (16)	–3719 (9)	112 (7)	C^{44}	–2502 (6)	–3678 (11)	–472 (9)	91 (6)
C^{12}	–2240 (8)	–2286 (14)	–3417 (14)	180 (12)	C^{45}	–904 (8)	–1474 (13)	–500 (13)	124 (9)
C^{13}	–1695 (9)	–4449 (19)	–3505 (13)	182 (14)	C^{46}	–364 (9)	–1587 (17)	264 (13)	194 (14)
C^{14}	–1901 (8)	–979 (19)	–1800 (16)	220 (2)	C^{47}	108 (9)	–1339 (13)	370 (13)	203 (14)
C^{15}	–1419 (8)	–815 (18)	–1852 (16)	210 (16)	C^{48}	68 (8)	–982 (14)	–300 (12)	127 (8)

[a] Determined as 1/3 of the trace of the orthogonalized $U_{i,j}$ tensor.

chem 5.1 software package. Structures corresponding to transition states of the rearrangement **V⇄VII** (1st rank saddle points) were checked by the existence of a single imaginary vibration frequency.

1-[*N*,*N*′-Diaryl-*N*-methoxycarbonyl-α-naphth(benz)amidinio-*N*′]-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienides (III). A solution of 0.004 mol of 5-nitro-1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (**I**) [16] in 60 ml of benzene was added with stirring to 0.008 mol of the corresponding amidine **II** [17] in 50 ml of benzene. The mixture was kept for 48 h at room temperature, and the solvent was removed under reduced pressure. The dark red residue was subjected to column chromatography on neutral aluminum oxide (eluent hexane–chloroform, 1 : 1). A fraction with R_f 0.8–0.9 (yellow spot) contained *N*-nitrosoamidine **IV**. A fraction with R_f 0.4–0.6 (red spot) contained ylide **III**. Recrystallization of the latter from benzene–hexane (1 : 2) gave red crystals. Yield 80–82%.

1-[*N*,*N*′-Diaryl-α-naphth(benz)amidinio-*N*′]-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienides V. Ylide **III**, 0.005 mol, was added to a solution of 0.005 mol of sodium hydroxide in 80 ml of methanol. The mixture was stirred for 1 h at 40° and cooled to 0°C, and 1 equiv of concentrated hydrochloric acid was added dropwise. The precipitate of NaCl was filtered off, the solvent was removed under reduced pressure, and the residue was recrystallized from benzene–hexane, 1 : 2. Yellow crystals. Yield 80–85%.

Tables 1 and 2 contain the melting points, data of elemental analysis, and IR and ^{1}H and ^{13}C NMR spectra of compounds **III** and **V**. The mass spectra of compounds **Va**–**Vc**, **Ve**, and **Vf**, *m*/*z* (I_{rel}, %), are given below.

Compound **Va**: 646 (6.7%) $[M]^+$, 616 (1.0) $[M-HCHO]^+$, 615 (2.6) $[M-OMe]^+$, 614 (1.9) $[M-MeOH]^+$, 602 (0.6) $[M-CO_2]^+$, 601 (1.4) $[M-OEt]^+$, 588 (0.7) $[M-MeCOMe]^+$, 587 (1.4) $[M-CO_2Me]^+$, 584 (0.3) $[M-2MeO]^+$, 583 (0.6) $[M-MeOH-OMe]^+$, 557 (0.4) $[M-CO_2Me-2Me]^+$, 556 (1.2) $[M-CO_2Me-OMe]^+$, 555 (2.9) $[M-C_6H_4Me\text{-}4]^+$, 540 (0.3) $[M-HNC_6H_4Me\text{-}4]^+$, 509 (0.7) $[M-HNC_6H_4Me\text{-}4-OMe]^+$, 508 (1.9) $[M-HNC_6H_4Me\text{-}4-$

MeOH]$^+$, 420 (0.3) [*M* – HNC_6H_4Me-4 – C_6H_4Me-4 – CHO]$^+$, 418 (0.4) [*M* – HNC_6H_4Me-4 – C_6H_4Me-4 – OMe]$^+$, 403 (0.2) [*M* – HNC_6H_4Me-4 – C_6H_4Me-4 – MeOMe]$^+$, 401 (0.7) [*M* – $C_{10}H_7CNHC_6H_4$Me-4]$^+$, 372 (0.2) [*M* – $C_{10}H_7CNHC_6H_4$Me-4 – CHO]$^+$, 371 (0.3) [*M* – $C_{10}H_7CNHC_6H_4$Me-4 – HCHO]$^+$, 339 (0.2) [*M* – $C_{10}H_7CNHC_6H_4$Me-4 – 2OMe]$^+$, 310 (0.7) [$NC_5(CO_2Me)_4$]$^+$, 307 (1.1) [4-Me$C_6H_4NC_5$–$(CO_2Me)_4$ – MeOH – 2OMe]$^+$, 245 (20.3) [$C_{10}H_7$-$CNHC_6H_4$Me-4]$^+$, 244 (100) [$C_{10}H_7CNC_6H_4$Me-4]$^+$, 127 (10.1) [$C_{10}H_7$]$^+$, 91 (22.9) [C_7H_7]$^+$, 77 (2.4) [Ph]$^+$, 65 (11.2) [C_5H_5]$^+$, 59 (3.0) [CO_2Me]$^+$, 32 (23.5) [MeOH]$^+$, 31 (33.1) [OMe]$^+$, 29 (25.8) [HCN]$^+$, 15 (14.8) [Me]$^+$.

Compound **Vb**: 646 (4.8%) [*M*]$^+$, 616 (0.6) [*M* – HCHO]$^+$, 615 (1.3) [*M* – OMe]$^+$, 614 (1.1) [*M* – MeOH]$^+$, 602 (0.2) [*M* – CO_2]$^+$, 601 (0.5) [*M* – OEt]$^+$, 588 (0.4) [*M* – MeCOMe]$^+$, 587 (0.8) [*M* – CO_2Me]$^+$, 584 (0.3) [*M* – 2OMe]$^+$, 583 (0.4) [*M* – MeOH – OMe]$^+$, 557 (0.3) [*M* – CO_2Me – 2Me]$^+$, 556 (0.8) [*M* – CO_2Me – OMe]$^+$, 555 (2.2) [*M* – C_6H_4Me-3]$^+$, 540 (0.1) [*M* – HNC_6H_4Me-3]$^+$, 509 (0.5) [*M* – HNC_6H_4Me-3 – OMe]$^+$, 508 (1.3) [*M* – HNC_6H_4Me-3 – MeOH]$^+$, 420 (0.1) [*M* – HNC_6H_4Me-3 – C_6H_4Me-3 – CHO]$^+$, 418 (0.2) [*M* – HNC_6H_4Me-3 – C_6H_4Me-3 – OMe]$^+$, 403 (0.7) [*M* – HNC_6H_4Me-3 – C_6H_4Me-3 – MeOMe]$^+$, 401 (0.8) [*M* – $C_{10}H_7$ – $CNHC_6H_4$Me-3]$^+$, 372 (0.7) [*M* – $C_{10}H_7$CNH – C_6H_4Me-3 – CHO]$^+$, 371 (2.8) [*M*-$C_{10}H_7$CNH – C_6H_4Me-3 – HCHO]$^+$, 339 (3.3) [*M* – $C_{10}H_7$CNH – C_6H_4Me-3 – 2OMe]$^+$, 310 (1.5) [$NC_5(CO_2Me)_4$]$^+$, 307 (9.3) [3-Me$C_6H_4NC_5$-$(CO_2Me)_4$ – MeOH – 2OMe]$^+$, 245 (19.5) [$C_{10}H_7$-$CNHC_6H_4$Me-3]$^+$, 244 (100) [$C_{10}H_7CNC_6H_4$Me-3]$^+$, 127 (6.3) [$C_{10}H_7$]$^+$, 91 (24.4) [C_7H_7]$^+$, 77 (3.0) [Ph]$^+$, 65 (10.2) [C_5H_5]$^+$, 59 (4.2) [CO_2Me]$^+$, 32 (33.4) [MeOH]$^+$, 31 (52.0) [OMe]$^+$, 29 (63.0) [HCN]$^+$, 15 (19.7) [Me]$^+$.

Compound **Vc**: 596 (10.0%) [*M*]$^+$, 580 (0.1) [*M* – CH_4]$^+$, 579 (0.3) [*M* – OH]$^+$, 567 (0.3) [*M* – CHO]$^+$, 566 (1.2) [*M* – HCHO]$^+$, 565 (3.0) [*M* – OMe]$^+$, 564 (1.3) [*M* – MeOH]$^+$, 552 (0.2) [*M* – CO_2]$^+$, 551 (0.6) [*M* – OEt]$^+$, 538 (0.4) [*M* – MeCOMe]$^+$, 537 (1.0) [*M* – CO_2Me]$^+$, 534 (0.2) [*M* – 2OMe]$^+$, 533 (0.4) [*M* – MeOH – OMe]$^+$, 519 (0.1) [*M* – Ph]$^+$, 507 (0.3) [*M* – CO_2Me – 2Me]$^+$, 506 (1.1) [*M* – CO_2Me – OMe]$^+$, 505 (3.2) [*M* – C_6H_4Me-4]$^+$, 490 (0.3) [*M* – HNC_6H_4-Me-4]$^+$, 459 (0.4) [*M* – HNC_6H_4Me-4 – OMe]$^+$, 458 (1.1) [*M* – HNC_6H_4Me-4 – MeOH]$^+$, 401 (0.4) [*M* – $PhCNHC_6H_4$Me-4]$^+$, 368 (0.6) [*M* – HNC_6H_4Me-4 – C_6H_4Me-4 – OMe]$^+$, 338 (0.3) [*M* – HNC_6H_4Me-4 – C_6H_4Me-4 – Me – MeOMe]$^+$, 311 (0.3) [HNC_5-$(CO_2Me)_4$]$^+$, 310 (1.0) [$NC_5(CO_2Me)_4$]$^+$, 308 (0.4) [(C_6H_4Me-4)$NC_5(CO_2Me)_4$–3OMe]$^+$, 307 (1.0) [(C_6H_4Me-4)$NC_5(CO_2Me)_4$ – MeOH – 2OMe]$^+$, 195 (16.4) [$PhCNHC_6H_4$Me-4]$^+$, 194 (100) [$PhCNC_6H_4$-Me-4]$^+$, 118 (2.8) [$CNHC_6H_4$Me-4]$^+$, 91 (27.4) [C_7H_7]$^+$, 77 (4.0) [Ph]$^+$, 65 (9.0) [C_5H_5]$^+$, 59 (3.0) [CO_2Me]$^+$, 32 (5.1) [MeOH]$^+$, 31 (9.5) [OMe]$^+$, 29 (6.9) [HCN]$^+$, 15 (7.5) [Me]$^+$.

Compound **Ve**: 630 (3.3%) [*M*]$^+$, 600 (1.1) [*M* – HCHO]$^+$, 599 (2.2) [*M* – OMe]$^+$, 598 (1.7) [*M* – MeOH]$^+$, 595 (0.2) [*M* – ^{35}Cl]$^+$, 574 (1.0) [*M* – 2CO]$^+$, 572 (3.3) [*M* – MeCOMe]$^+$, 571 (5.4) [*M* – CO_2Me]$^+$, 540 (0.7) [*M* – CO_2Me – OMe]$^+$, 539 (1.0) [*M* – C_6H_4Me-4]$^+$, 524 (0.9) [*M* – HNC_6H_4Me-4]$^+$, 519 (1.7) [*M* – $C_6H_4{}^{35}$Cl-2]$^+$, 433 (2.1) [*M* – HNC_6H_4-Me-4 – C_6H_4Me-4]$^+$, 401 (5.2) [*M* – 2-$^{35}ClC_6H_3$CNH-C_6H_4Me-4]$^+$, 310 (0.7) [$NC_5(CO_2Me)_4$]$^+$, 229 (17.4) [2-$^{35}ClC_6H_4CNHC_6H_4$Me-4]$^+$, 228 (100) [2-^{35}Cl-$C_6H_4CNC_6H_4$Me-4]$^+$, 193 (12.4) [2-$^{35}ClC_6H_4$CN-C_6H_4Me-4-^{35}Cl]$^+$, 152 (82.6) [$NCNHC_6H_4{}^{35}$Cl-2]$^+$, 139 (63.3) [$H_2NCHC_6H_4{}^{35}$Cl-2]$^+$, 111 (16.0) [C_6H_4-^{35}Cl-2]$^+$, 91 (29.8) [C_7H_7]$^+$, 65 (8.3) [C_5H_5]$^+$, 59 (3.7) [CO_2Me]$^+$, 32 (66.2) [MeOH]$^+$, 31 (94.6) [OMe]$^+$, 29 (99.7) [HCN]$^+$, 15 (47.0) [Me]$^+$.

Compound **Vf**: 676 (6.4%) [*M*]$^+$, 646 (1.0) [*M* – HCHO]$^+$, 645 (2.8) [*M* – OMe]$^+$, 644 (3.7) [*M* – MeOH]$^+$, 632 (0.6) [*M* – CO_2]$^+$, 631 (1.6) [*M* – OEt]$^+$, 630 (1.0) [*M* – EtOH]$^+$, 618 (0.6) [*M* – MeCOMe]$^+$, 617 (1.6) [*M* – CO_2Me]$^+$, 613 (1.0) [*M* – MeOH – OMe]$^+$, 595 (3.7) [*M* – ^{81}Br]$^+$, 586 (1.5) [*M* – CO_2Me – OMe]$^+$, 585 (3.7) [*M* – C_6H_4Me-4]$^+$, 570 (1.8) [*M* – HNC_6H_4Me-4]$^+$, 503 (0.8) [*M* – ^{81}Br – C_6H_4Me-4]$^+$, 401 (1.3) [*M* – 2-$^{81}BrC_6H_4CNHC_6H_4$Me-4]$^+$, 310 (1.5) [$NC_5(CO_2Me)_4$]$^+$, 275 (7.4) [2-$^{81}BrC_6H_4CNHC_6H_4$-Me-4]$^+$, 274 (48.6) [2-$^{81}BrC_6H_4CNC_6H_4$Me-4]$^+$, 194 (2.4) [2-$^{81}BrC_6H_4CNHC_6H_4$Me-4 – ^{81}Br]$^+$, 193 (4.2) [2-$^{81}BrC_6H_4CNC_6H_4$Me-4 – ^{81}Br]$^+$, 118 (2.0) [$CNHC_6H_4$Me-4]$^+$, 91 (100) [C_7H_7]$^+$, 82 (2.7) [H^{81}Br]$^+$, 77 (4.0) [Ph]$^+$, 65 (37.1) [C_5H_5]$^+$, 59 (14.4) [CO_2Me]$^+$, 32 (67.4) [MeOH]$^+$, 31 (92.0) [OMe]$^+$, 29 (75.1) [HCN]$^+$, 15 (51.0) [Me]$^+$.

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