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Synthesis and Structure of 5,5'-[(*E*,*E*)-2,5-Diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one)

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Abstract—Treatment of 2,3,5-trichloro-5-[(*E*)-2,3-diiodoprop-1-en-1-yl]-4,4-dimethoxycyclopent-2-en-1-one with SmI_2 in THF gives 5,5'-[(1*E*,5*E*)-2,5-diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one) and its *meso* form at a ratio of 3 : 1.

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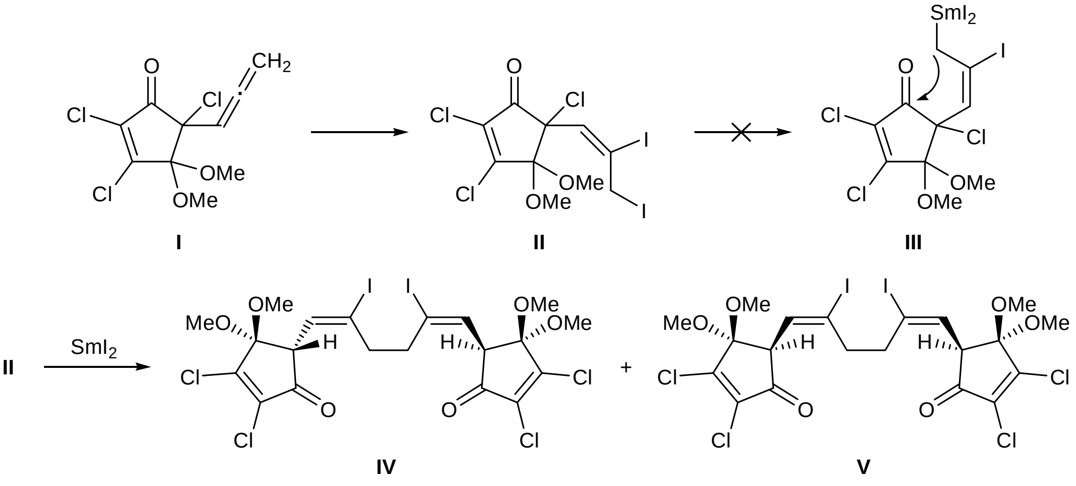
Samarium(II) iodide is widely used as one-electron reducing agent in synthetic organic chemistry; it ensures high chemoselectivity in most transformations [1, 2]. We previously [3] synthesized vicinal diiodo derivative **II** from allenyltrichlorocyclopentenone **I** [4]; compound **II** may be regarded as a specific reaction partner in SmI_2-initiated tandem transformations [5, 6]. Among several versions possible for the reaction of this multident electrophile, we were primarily interested in effecting Barbier-type intramolecular coupling which begins with generation of the corresponding allylic samarium(III) intermediate **III** via reaction at the most preferred fragment in allyl iodide **II** (Scheme 1). We believed that the probability for ring closure in intermediate **III** through 1,2-addition at the accessible keto group should be fairly high.

However, experiments showed that the reaction of diiodide **II** with 2.2 equiv of SmI_2 was very fast, the conversion of compound **II** was not complete (about 50%), and two new products were formed at a ratio of 3 : 1 (according to the ^{1}H NMR data). The complete conversion of **II** was attained in the reaction with 4.4 equiv of SmI_2, and we isolated in more than 80% yield a 3 : 1 mixture of isomeric compounds (^{1}H NMR data) which were difficult to separate by chromatography on silica gel. We succeeded in isolating the

Scheme 1.



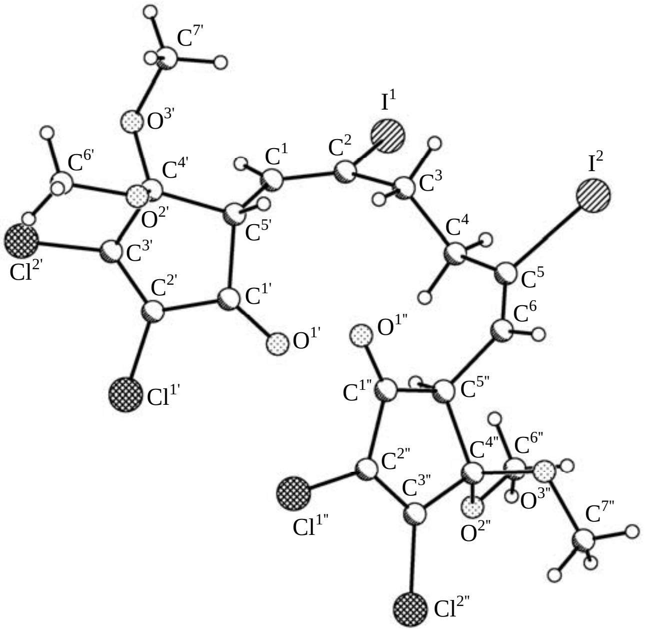


Fig. 1. Structure of the molecule of (5*RS*,5'*RS*)-5,5'-[(1*E*,5*E*)-2,5-diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-di-methoxycyclopent-2-en-1-one) (**IV**) according to the X-ray diffraction data.

major isomer as individual substance by recrystallization from petroleum ether–ethyl acetate (95:5). On the basis of the ^{1}H and ^{13}C NMR and mass spectra, it was assigned structure **IV** which was then proved by X-ray analysis (Fig. 1). The isolated crystalline dimer **IV** was a racemate (*RR*+*SS*). Presumably, the minor isomer (**V**) is a *meso* form (*RS*+*SR*).

According to the X-ray diffraction data, compound **IV** is a 1,2-substituted ethane with *anti* arrangement of two similar substituents having a complex structure (the torsion angle $C^2C^3C^4C^5$ is 172.7°). The bond lengths and bond angles in molecule **IV** do not differ from those typical of structurally related compounds. An exception is that the cyclopentenone fragments in the two parts of the molecule have different geometric parameters (see table). Both cyclopentene rings adopt an envelope conformation, but the $C^{5'}$ atom deviates from the $C^{1'}C^{2'}C^{3'}C^{4'}$ plane by 0.415 Å, while the $C^{5''}$ atom in the other ring deviates from the $C^{1''}C^{2''}C^{3''}C^{4''}$ plane by only 0.288 Å, i.e., in the latter case the cyclopentene ring is flatter.

Molecules **IV** in crystal are packed in layers (Fig. 2). Numerous intermolecular contacts between the halogen atoms should be noted. The main structural fragment of the crystal packing consists of chains formed via two pairs of strong contacts $Cl^{1'}\cdots Cl^{1''A}$/$Cl^{1''}\cdots Cl^{1'A}$ [$1 - x, 1 - y, -z$] and $I^1\cdots Cl^{2'B}$/$Cl^{2'}\cdots I^{1B}$ [$-x, -y, -z$], as follows from shortened interatomic distances Cl···Cl 3.355(2) Å and I···Cl 3.620(2) Å (the sums of the corresponding van der Waals radii are 3.65 and 3.88 Å, respectively) [7]. A combination of these chains gives a layer ([110] plane) mainly through strong $I^2\cdots Cl^{2'C}$ interactions [d = 3.622(2) Å; $x, y, 1 + z$]]. The layers are linked to each other through much weaker Cl···H–C and I···H–C contacts; these contacts are only slightly shorter than the corresponding normal van der Waals contacts, 2.97 and 3.14 Å, respectively [7].

Thus compound **IV** in crystal may be regarded as a supramolecular assembly [8] having a layered structure with zigzag chains as the principal fragment, which is formed due to numerous intermolecular interactions between the halogen atoms. These data are consistent with those reported in [9]: provided that a molecule contains two halogen atoms, the formation of Hlg-aggregates including more than two molecules is a typical pattern. The difference in the degree of

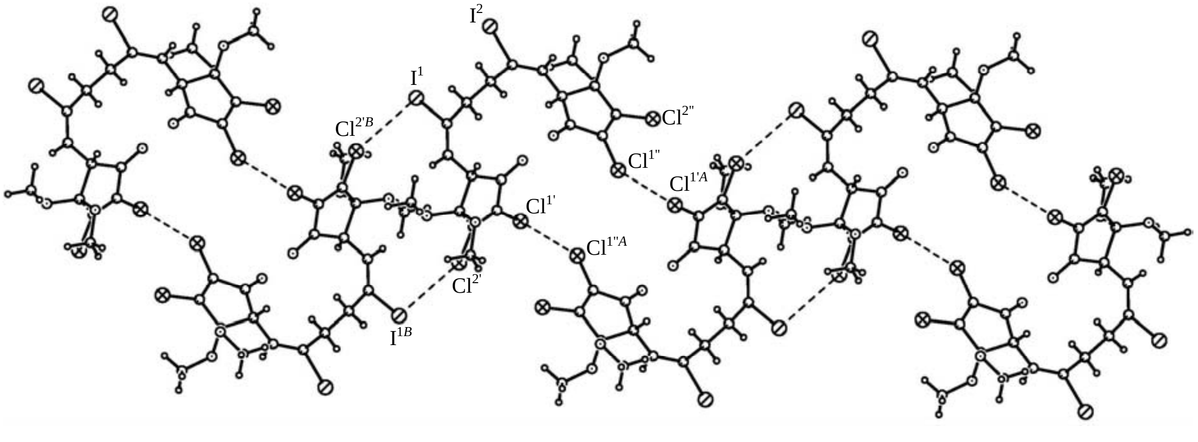


Fig. 2. Molecular chains in the crystalline structure of (5*RS*,5'*RS*)-5,5'-[(1*E*,5*E*)-2,5-diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one) (**IV**).

flattening of the cyclopentene rings in molecule **IV** is likely to result from their *anti* arrangement at the ends of the diiodohexadiene bridge; molecular chains in the crystal packing may be characterized by some distortion of coplanarity and differences in spatial orientation of intermolecular contacts between the halogen atoms in the cyclopentene rings.

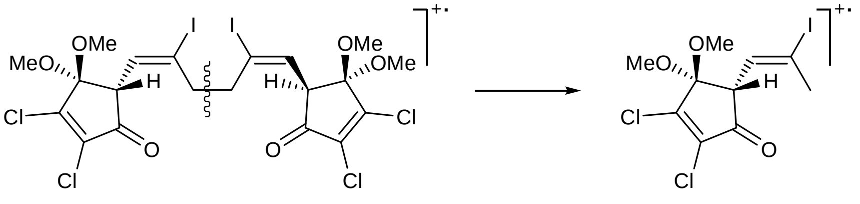
The ^{1}H and ^{13}C NMR signals of minor isomer **V** were identified from the spectrum of mixture **IV**/**V** (3:1). The largest differences in the ^{13}C chemical shifts between stereoisomers **IV** and **V** were observed for C^3, C^4 ($\Delta\delta_C$ = 1.16 ppm), and C^5 ($\Delta\delta_C$ 0.38 ppm); the differences for the other atoms did not exceed 0.2 ppm. The ^{1}H NMR spectrum of a solution of mixture **IV**/**V** in $CDCl_3$ contained a doublet at δ 6.25 ppm from protons at the double bond (1-H, 6-H) in the bridging group of both isomers. The difference between the chemical shifts of 5'-H and 5''-H was Δδ = 0.02 ppm, and the CH_2CH_2 protons gave a complex multiplet in the region δ 2.85–2.70 ppm. Appreciable differences between proton chemical shifts of the racemate and *meso* form **V** were revealed in the ^{1}H NMR spectra of a mixture of **IV** and **V** and pure **IV** in CCl_4–C_6D_6 (1:1). Here, the doublet signal from 5'-H of the major isomer was located at δ 3.9 ppm, and that of the minor isomer, at δ 3.77 ppm. Diastereotopic protons in the CH_2CH_2 fragment of the major isomer gave two distorted triplets with equal intensities at δ 2.91 and 2.78 ppm (^{2}J = 13.2, ^{3}J = 11.4 Hz). The corresponding methylene protons of the minor isomer are characterized by similar chemical shifts, and they appear as one multiplet at δ ~2.8 ppm.

Some bond lengths (*d*) and bond (ω) and dihedral angles (φ) in the cyclopentenone fragments of the molecule of (5*RS*,5'*RS*)-5,5'-[(1*E*,5*E*)-2,5-diiodohexa-1,5-diene-1,6-diyl]-bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one) (**IV**)

Bond	*d*, Å	Bond	*d*, Å
$C^{1'}–C^{2'}$	1.479(7)	$C^{1''}–C^{2''}$	1.484(8)
$C^{2'}–C^{3'}$	1.325(7)	$C^{2''}–C^{3''}$	1.337(9)
$C^{3'}–C^{4'}$	1.529(7)	$C^{3''}–C^{4''}$	1.508(7)
$C^{4'}–C^{5'}$	1.561(7)	$C^{4''}–C^{5''}$	1.554(7)
$C^{5'}–C^{1'}$	1.537(7)	$C^{5'}–C^{1''}$	1.545(7)
$C^{1'}–O^{1'}$	1.204(6)	$C^{1''}–O^{1''}$	1.193(7)
$C^{4'}–O^{2'}$	1.412(6)	$C^{4''}–O^{2''}$	1.411(6)
$C^{4'}–O^{3'}$	1.386(6)	$C^{4''}–O^{3''}$	1.417(6)
$C^{2'}–Cl^{1'}$	1.719(5)	$C^{2''}–Cl^{1''}$	1.700(6)
$C^{3'}–C^{2'}$	1.710(5)	$C^{3''}–Cl^{2''}$	1.709(6)
$C^{5'}–C^{1}$	1.519(7)	$C^{5''}–C^{6}$	1.513(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
$C^{1'}C^{2'}C^{3'}$	110.5(5)	$C^{1''}C^{2''}C^{3''}$	110.3(5)
$C^{2'}C^{3'}C^{4'}$	112.2(4)	$C^{2''}C^{3''}C^{4''}$	113.3(5)
$C^{3'}C^{4'}C^{5'}$	101.4(4)	$C^{3''}C^{4''}C^{5''}$	103.0(4)
$C^{4'}C^{5'}C^{1'}$	103.1(4)	$C^{4''}C^{5''}C^{1''}$	104.5(4)
$C^{5}C^{1'}C^{2'}$	105.8(4)	$C^{5''}C^{1''}C^{2''}$	105.7(5)
Angle	**φ, deg**	**Angle**	**φ, deg**
$C^{1'}C^{2'}C^{3'}C^{'4'}$	5.4(6)	$C^{1''}C^{2''}C^{3''}C^{4''}$	1.8(7)
$C^{2'}C^{3'}C^{4'}C^{5'}$	19.9(5)	$C^{2''}C^{3''}C^{4''}C^{5''}$	9.6(6)
$C^{3'}C^{2'}C^{1'}C^{5'}$	12.0(6)	$C^{3''}C^{2''}C^{1''}C^{5''}$	12.6(6)
$C^{3'}C^{2'}C^{1'}O^{1'}$	–172.2(5)	$C^{3''}C^{2''}C^{1''}O^{1''}$	–169.1(6)
$C^{4'}C^{3'}C^{2'}Cl^{1'}$	–174.1(4)	$C^{4''}C^{3''}C^{2''}Cl^{1''}$	179.7(4)
$C^{1'}C^{2'}C^{3'}Cl^{2'}$	177.0(4)	$C^{1''}C^{2''}C^{3''}Cl^{2''}$	–179.5(5)
$C^{2'}C^{3'}C^{4'}O^{2'}$	–91.0(5)	$C^{2''}C^{3''}C^{4''}O^{2''}$	130.5(5)
$C^{2'}C^{3'}C^{4'}O^{3'}$	143.3(5)	$C^{2''}C^{3''}C^{4''}O^{3''}$	–105.2(6)

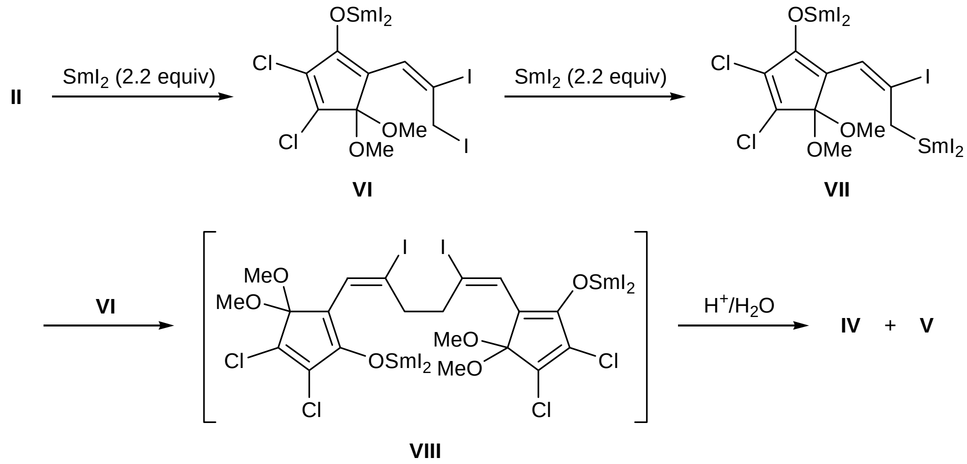
The molecular and fragment ion peaks present in the high-resolution mass spectrum of **IV** reflect well structural specificity of this compound. The intensity distribution in the molecular ion cluster, $[M]^+$: $[M + 2]^+$:$[M + 4]^+$ = 0.76:1:0.48, corresponds to the presence of four chlorine atoms. The exact *m*/*z* value is consistent with the composition $C_{20}H_{20}{}^{35}Cl_4I_2O_6$ (*m*/*z* 749.812 a.m.u.; calculated 749.810 a.m.u). The heaviest fragment ions are formed as a result of elimination of halogen atoms and methoxy groups from the molecular ion: *m*/*z* 714.843 $[M – Cl]^+$, 627.901 $[M – I]^+$, 717.791 $[M – OCH_3]^+$, 686.764 $[M – OCH_3 – HOCH_3]^+$, 590.879 $[M – I – HOCH_3]^+$. This fragmentation pattern is typical of compounds containing halogen atoms and methoxy groups [10]. The most abundant fragment

Scheme 2.



$[M]^+$, *m*/*z* 749.812 (I_{rel} 9.2%) *m*/*z* 374.905 (I_{rel} 100%)

Scheme 3.



ion is $C_{10}H_{10}{}^{35}Cl_2IO_3$ (*m*/*z* 374.905); it is formed via energetically favorable cleavage of the allylic C–C bond [11] (Scheme 2).

Probable mechanistic aspects of the formation of compounds **IV** and **V** are illustrated by Scheme 3. The absence among the products of expected intra- or intermolecular 1,2-adducts at the carbonyl group and the formation of only dimers **IV** and **V** via dechlorination at C^5, as well as the consumption of 4.4 equiv of SmI_2, indicate that the process involves initial reductive enolization to give samarium enolate **VI**, which prevents formation of compound **III**. Unlike enone **II**, the allylic iodine atom in the cross-conjugated system of enol **VI** is highly reactive; therefore, intermediate **VI** is quickly converted (*in statu nascendi*) into secondary intermediate **VII**, and the latter reacts with **VI** to form Wurtz coupling product **VIII**. This is the reason why allyl iodide **II** is not involved in cross reactions with **VII**, for it is consumed exclusively through enolate **VI**.

The lack of any significant stereocontrol is responsible for nonstereoselective protonation of the planar cyclopentadiene rings in molecule **VIII**. The observed stereoisomer ratio (**IV**:**V** = 3:1) is likely to be determined only by specificity of the transition state, e.g., by product-forming control [12] or some other factors.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 spectrometers from samples prepared as thin films or dispersed in mineral oil. The NMR spectra were measured on a Bruker AM-300 instrument at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C relative to the solvent signals ($CDCl_3$: δ 7.27, δ_C 77.00 ppm). The mass spectra were obtained on a Thermo Finnigan MAT-95P mass spectrometer (electron impact, 70 eV; ion source temperature 200°C; samples were injected at 50–270°C; temperature ramp 22 deg/min). The progress of the reaction was monitored by TLC on Silufol plates using petroleum ether–ethyl acetate; spots were visualized by treatment with an alkaline solution of potassium permanganate [13].

Reaction of 2,3,5-trichloro-5-[(*E*)-2,3-diodoprop-1-en-1-yl]-4,4-dimethoxycyclopent-2-en-1-one (II) with SmI_2 in THF. A 0.03 M solution of enone **II** in THF, 12 ml (0.37 mmol), was added to 16 ml (1.6 mmol) of a 0.1 M solution of SmI_2 in THF, cooled to –60°C, under stirring in a stream of argon. The mixture was allowed to warm up to –35°C, kept for 1.5 h at that temperature, treated with 5 ml of a 5% solution of sodium hydrogen carbonate, and extracted with ethyl acetate (3×25 ml). The extracts were washed with water and a saturated solution of sodium chloride, dried over $MgSO_4$, concentrated, and subjected to chromatography on silica gel using petroleum ether–ethyl acetate (8:2) as eluent to isolate 0.13 g (83%) of stereoisomer mixture **IV**/**V** at a ratio of 3:1 (according to the ^1H NMR data).

(5*RS*,5'*RS*)-5,5'-[(1*E*,5*E*)-2,5-Diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one) (IV). Colorless crystals, mp 138–139.5°C (from petroleum ether–ethyl acetate, 95:5), R_f 0.39 (petroleum ether–ethyl acetate, 95:5; double elution). IR spectrum, ν, cm^{-1}: 988, 1066, 1150, 1198, 1200, 1600, 1732. ^1H NMR spectrum, δ, ppm: in $CDCl_3$: 2.70–2.85 m (2H, 3-H_A, 4-H_A), 2.85–3.00 m (2H, 3-H_B, 4-H_B), 3.42 s (6H, OCH_3), 3.49 s (6H, OCH_3), 4.87 d (2H, 5'-H, 5"-H, *J* = 9.2 Hz), 6.25 d (2H, 1-H, 6-H, *J* = 9.2 Hz); in C_6D_6–CCl_4 (1:1): 2.78 d.d (2H, 3-H_A, 3-H_A, ^2J = 13.2, ^3J = 11.4 Hz), 2.91 d.d (2H, 3-H_B, 4-H_B, ^2J = 13.2, ^3J = 11.4 Hz), 3.26 s (6H, OCH_3), 3.43 s (6H, OCH_3), 3.90 d (2H, 5'-H, 5''-H, J = 9.3 Hz), 6.29 d (2H, 1-H, 6-H, J = 9.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.13 (C^3, C^4), 51.87 and 57.92 (OCH_3), 57.92 ($C^{5'}$, $C^{5''}$), 102.05 (C^2, C^5), 105.72 ($C^{4'}$, $C^{4''}$), 132.12 (C^1, C^6), 134.30 ($C^{2'}$, $C^{2''}$), 158.67 ($C^{3'}$, $C^{3''}$), 190.45 ($C^{1'}$, $C^{1''}$). Mass spectrum, m/z (I_{rel}, %): $[M]^+$ 750 (9.2), 752 (12.1), 754 (5.8), 715 (0.3), 719 (0.4), 685 (1.2), 591 (10.9), 375 (100), 235 (29.1), 233 (43.3), 197 (17.6). Found, %: C 31.88; H 2.52; Cl 20.39. $C_{20}H_{20}Cl_4I_2O_4$. Calculated, %: C 31.94; H 2.68; Cl 18.86.

(5*RS*,5'*SR*)-5,5'-[(1*E*,5*E*)-2,5-Diiodohexa-1,5-diene-1,6-diyl]bis(2,3-dichloro-4,4-dimethoxycyclopent-2-en-1-one) (V). Colorless oily substance, R_f 0.26 (petroleum ether–ethyl acetate, 95:5; double elution). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 2.7–2.85 m (4H, CH_2CH_2), 3.43 (6H, OCH_3), 3.49 s (6H, OCH_3), 4.85 d (2H, 5'-H, 5''-H, J = 9.2 Hz), 6.25 d (2H, 1-H, 6-H, J = 9.2 Hz); in C_6D_6–CCl_4 (1:1): 2.75–2.85 m (4H, CH_2CH_2), 3.27 (6H, OCH_3), 3.34 s (6H, OCH_3), 3.77 d (2H, 5'-H, 5''-H, J = 9.3 Hz), 6.28 d (2H, 1-H, 6-H, J = 9.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.02 (C^3, C^4), 52.19 (OCH_3), 58.29 ($C^{5'}$, $C^{5''}$), 102.22 (C^2, C^5), 106.01 ($C^{4'}$, $C^{4''}$), 132.35 (C^1, C^6), 134.52 ($C^{2'}$, $C^{2''}$), 158.36 ($C^{3'}$, $C^{3''}$), 189.87 ($C^{1'}$, $C^{1''}$).

X-Ray diffraction study of compound (IV). Colorless needles. $C_{20}H_{20}Cl_4I_2O_6$. M 751.96. Triclinic crystals, space group $P1$, crystal habit 0.2 × 0.05 × 0.03 mm; a = 9.023(2), b = 11.107(2), c = 87.573(4) Å; α = 87.573(4), β = 88.108(4), γ = 74.436 (4)°; V = 128.3(4) Å^3; Z = 2; μ = 2.893 mm^{-1}; d_{calc} = 1.941 g × cm^{-3}. Intensities of 10334 reflections were measured on a Bruker SMART CCD 1000 diffractometer at 120 K. Averaging of equivalent reflections gave 5502 independent reflections with R_{int} = 0/0262. The data were processed using SAINT Plus [14] and SADABS software packages [15]. The structure was refined by the direct method and consecutive electron density syntheses. All non-hydrogen atoms were localized from the electron density maps. The structure was refined by F^2_{hkl} in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms. The positions of the latter were calculated from geometry considerations and were involved in the refinement procedure using the *rider* model; $U(H_{iso}) = 1.2\,U(C_{eq})$, where $U(C_{eq})$ is the equivalent temperature factor of the carbon atom to which the corresponding hydrogen atom is attached. The final divergence factors were R^1 = 0.0489 [calculated by F^2_{hkl} from 4313 reflections with $I > \sigma(I)$] and wR^2 = 0.1299 (calculated by F^2_{hkl} from all 5502 reflections); number of refined parameters 289. All calculations were performed using SHELXTL software, version 5.10 [16]. The complete set of crystallographic data (coordinates of atoms, bond lengths, bond angles, and temperature factors) was deposited to the Cambridge Crystallographic Data Center.

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