

Novel organic luminophores with benzene-1,3,5-triyl branching units

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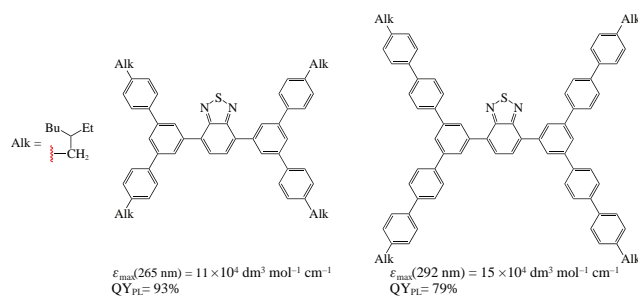
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Synthesis and examination of two highly luminescent oligophenylene derivatives of 2,1,3-benzothiadiazole with branching centers based on benzene-1,3,5-triyl units are described. These studies in combination with DFT calculations have shown that the presence of the branching centers causes differences in the absorption characteristics and similarity of the emission properties. High molar extinction coefficients (up to $15 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the medium UV-range and blue-green emission with quantum yields of 79–93% make them promising components of wavelength-shifting materials for optical devices.



Keywords: absorption spectrum, fluorescence spectrum, fluorescence quantum yield, organic luminophore, cross-coupling, benzene-1,3,5-triyl, oligophenylenes, 2,1,3-benzothiadiazole, DFT calculations.

Complex organic compounds consisting of a large number of π -conjugated atomic groups (chromophores) intensively absorb light in the visible and near UV range. They are widely used in photovoltaics,¹ biomedicine,² analytical chemistry,³ ionizing radiation detectors,⁴ photocatalysts.⁵ The absorption and fluorescence spectra of such compounds depend on the number, relative position and chemical structure of the chromophores.⁶ The position and intensity of the absorption bands are determined by the total length and shape of the π -electron system: the greater the length of the π -electron system, the more intense the absorption has a compound. To obtain a compound with a large absorption cross-section in a given spectral region, it is necessary to combine as many π -conjugated chromophores in one structure as possible. However, this is not enough since it is necessary to select the chemical structure of chromophores and the configuration of the compound, which should provide the required absorption and luminescent characteristics.

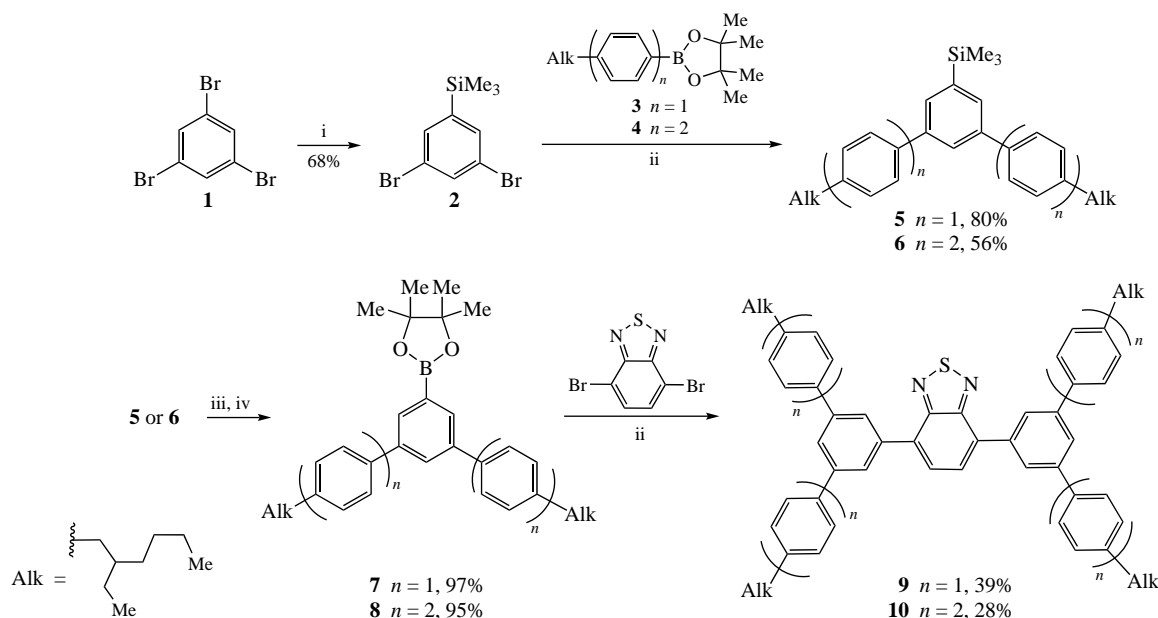
Intense absorption in a given spectral range can be provided by connecting groups of chromophores (conjugated fragments) through silicon, carbon or boron atoms, which isolate their π -electron systems from each other.^{7–10} The absorption spectra of such compounds correspond to the sum of the absorption spectra of isolated fragments. The emission characteristics are determined mainly by the chemical structure and configuration of moieties with narrow bandgap.

Creation of branched molecules without distortion of π -electron conjugation between chromophores is another way to achieve an intense absorption in a given spectral range. The branching centers in such molecules are usually molecular fragments of truxene,¹¹ benzene¹² or nitrogen atoms.¹³ The synthesis and photophysical properties of three branched compounds based on benzene-1,3,5-triyl units were described

previously.¹⁴ Each of these compounds contained in the acceptor part 2,1,3-benzothiadiazole equipped with two branching centers of 1,3,5-trisubstituted benzene moiety, while the donor contained from four to eight thiophene fragments. Those compounds intensively absorbed radiation in the medium UV region but had low fluorescence quantum yields, which should limit the possibilities of their application.

In this paper, two new 2,1,3-benzothiadiazole-type luminophores with branching centers based on 1,3,5-trisubstituted benzene are proposed and synthesized (Scheme 1). A lot of derivatives of 2,1,3-benzothiadiazole have a plenty of characteristics of ideal luminophores: a large Stokes shift, high chemical resistance, the ability to fine-tuning spectral properties by varying substituents, and relatively simple synthesis.^{15–18} Phenyl and biphenyl substituents are introduced into the *meta*-positions to achieve a high absorption cross-section in the middle and near UV range. Branched 2-ethylhexyl groups are added to the structures of molecules to increase their solubility.

Firstly, (3,5-dibromophenyl)trimethylsilane¹⁹ **2**, obtained by monolithiation of 1,3,5-tribromobenzene **1** with butyllithium followed by treatment with chloro(trimethyl)silane, was reacted with organoboron derivatives^{13,20} **3** or **4** to afford precursors **5** and **6** via Suzuki coupling (see Scheme 1). These compounds contained reactive trimethylsilyl functional groups. Secondly, the trimethylsilyl groups of compounds **5** and **6** were replaced by the pinacol boronate group by treating them with boron tribromide followed by hydrolysis and esterification with pinacol thus giving almost quantitative yields of products **7** and **8**. Finally, their Suzuki cross-coupling with 4,7-dibromo-2,1,3-benzothiadiazole¹⁶ afforded the target luminophores 4,7-bis(4,4''-bis(2-ethylhexyl)[1,1':3'1''-terphenyl]-5'-yl)-2,1,3-benzothiadiazole **9** and 4,7-bis(4,4''''-bis(2-ethylhexyl)[1,1':4'1''':3'',1'']-



Scheme 1 Reagents and conditions: i, BuLi, Et₂O, -78 °C, then Me₃SiCl; ii, Pd(PPh₃)₄, Na₂CO₃ (aq.), EtOH, PhMe, Δ; iii, BBr₃, CCl₄; iv, pinacol, PhH, 50 °C.

4'''',1''''-quinquephenyl]-5''-yl)-2,1,3-benzothiadiazole **10** in 39 and 28% yields, respectively (see Scheme 1 and Figure 1). Model reference compound 4,7-bis(4-trimethylsilylphenyl)-2,1,3-benzothiadiazole **11** (see Figure 1) was synthesized from an organoboron derivative of benzene with a trimethylsilyl group and 4,7-dibromo-2,1,3-benzothiadiazole by the Suzuki cross-coupling reaction as reported previously.¹⁴

The full structures of new and model compounds whose properties were further studied are shown in Figure 1. The absorption and fluorescence spectra of diluted solutions of new

luminophores **9**, **10** in THF and those of model compounds **5**, **6**, **11** are presented in Figure 2 and their main spectral characteristics are given in Table 1. Central fragments of 4,7-diphenyl-2,1,3-benzothiadiazole (green background), and peripheral terphenyl or quinquephenyl fragments (outlined with purple lines) can be distinguished in the structures of compounds **9**, **10** (see Figure 1) similarly to the thiophene-containing luminophores with benzene-1,3,5-triyl branching center studied previously.¹⁴ The central and peripheral fragments of the herein molecules contain the same branching centers. The spectral distribution of the

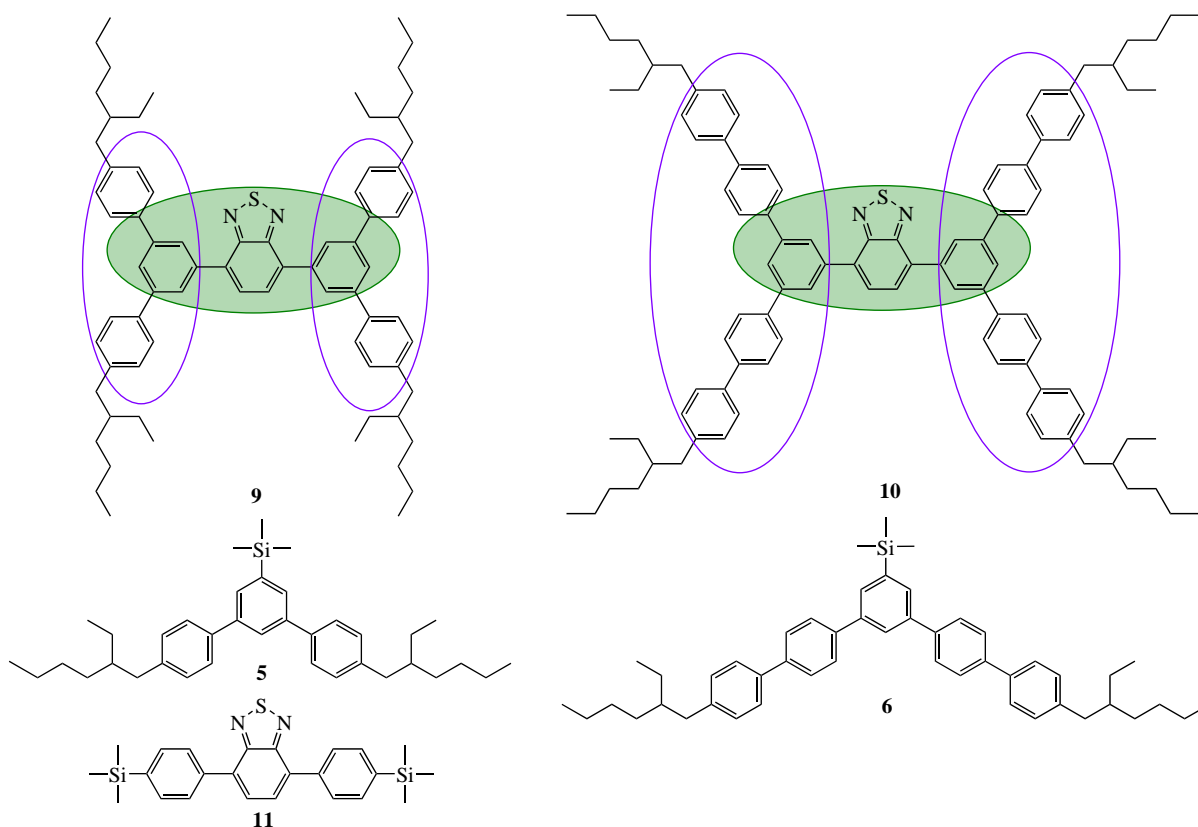


Figure 1 Structural formulas and designations of new luminophores and model compounds. Fragments of compounds with common molecular orbitals are highlighted by ovals.

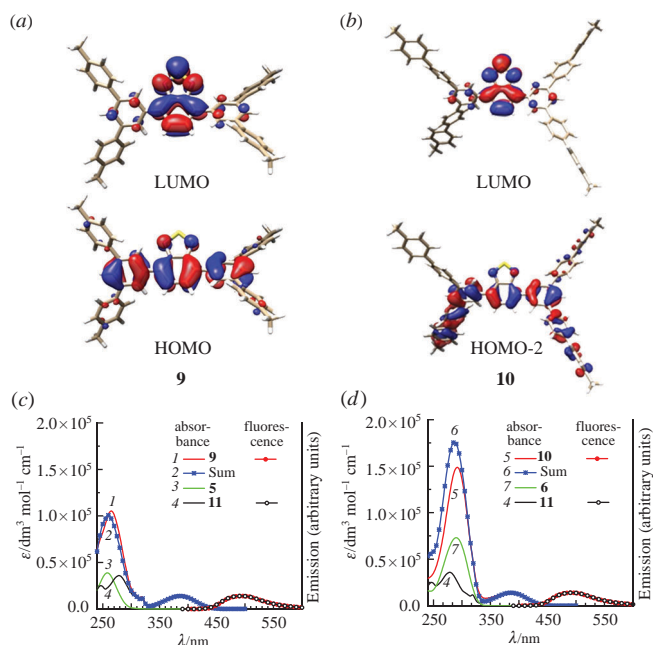


Figure 2 Spatial distribution of frontier molecular orbitals of (a) compound **9** and (b) compound **10**. Absorption and luminescence spectra of dilute solutions in THF for (c) compound **9** and (d) compound **10** and some model compounds. Curves 2 and 6 show the total spectral distribution $\epsilon(\lambda)$ of the corresponding peripheral (multiplied by 2) and central fragments.

molar extinction coefficient $\epsilon(\lambda)$ of compounds **9**, **10** is located in the wavelength range of 330–440 nm, which is close to that observed for compound **11** modeling the central fragment. In the wavelength range of 230–330 nm, the absorption spectra of **9**, **10** differ both from the spectrum of model compound **11** and from the spectra of precursors **5**, **6** modeling peripheral fragments. The calculated dependences of the molar extinction coefficients on the wavelength obtained by summing the spectral distributions of the extinction coefficients of **11** with doubled values of the extinction coefficients for **5** or **6** are close to the experimental data for compounds **9** and **10** [Figure 2(c),(d)]. Frontier molecular orbitals of compounds **9** and **10** according to the DFT quantum-chemical calculations²¹ are shown in Figure 2(a),(b). The distribution of some other orbitals, as well as characteristics of main electronic transitions, are given in Online Supplementary Materials (Figures and Tables S16–S19).

Comparison of model and experimental spectral distributions of **9** and **10** molar extinction coefficients with the results of quantum-chemical calculations shows that the absorption bands of synthesized compounds are formed by transitions between molecular orbitals localized mainly on fragments of

4,7-diphenyl-2,1,3-benzothiadiazole, **5** and **6**, similar to how it was established previously.¹⁴ The long wavelength absorption band in the spectrum of compound **9** is formed by transitions between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), covering mainly 2,1,3-benzothiadiazole and branching aromatic nuclei. The transition between HOMO-2 and LUMO of compound **10** is the most intense in the area under consideration, according to DFT calculations. The conventional transition between HOMO and LUMO is forbidden due to their poor overlap. Short wavelength absorption bands are caused by transitions between molecular orbitals, mainly localized on the peripheral ter- or quinquephenyl fragments of **5** or **6**.

The fluorescence spectra of compounds **9** and **10** are close to the fluorescence spectrum of the model compound **11**. Consequently, the LUMO corresponding to the lowest excited state from which fluorescence occurs is localized on the central fragments of compounds **9**, **10**. The shape of the spectrum, as well as the quantum yield^{22,23} of fluorescence (within the measurement error of $\pm 5\%$), do not depend on the wavelength of the excitation. This indicates a high probability of internal conversion between higher excited electronic states corresponding to peripheral fragments and the fluorescent state. The fluorescence quantum yield is 93% for **9** and 79% for **10**. These values are somewhat less than that for **11** approaching 96%. At the same time, the quantum yield of compounds with benzene-1,3,5-triyl branching centers and four peripheral thiophene groups was 33%, and with four bithiophene groups slightly exceeded 1%.¹³ Measurements of fluorescence lifetime allowed us to calculate the values of the radiative (k_r) and non-radiative (k_{nr}) constants for **9** and **10**. It was found that the values k_r were the same (see Table 1), while the value of k_{nr} for **9** was three times less than that for **10**, which explains the higher fluorescence quantum yield for the first compound.

The thermal stability in air of the synthesized luminophores was studied by thermogravimetry (TGA). Both compounds have sufficiently high thermal stability for processing into luminescent products based on optically transparent polymers and do not lose mass when heated in air to $>300^\circ\text{C}$. However, the temperature of 5% mass loss of the luminophore **9** exceeds the similar characteristic of the luminophore **10** by 69°C (406°C vs. 337°C). The developed luminophores are more thermally stable than their previously described analogs with thiophene peripheral fragments.¹⁴ Both new luminophores would crystallize and melt without degradation (differential scanning calorimetry (DSC) data). The melting points of **9** and **10** are 79°C and 192°C , respectively. The TGA and DSC curves are given in Online Supplementary Materials (Figures S14–S15).

To conclude, two new organic luminophores **9** and **10** were synthesized. They contain four phenyl or biphenyl donor chromophores, respectively, connected to the central acceptor 2,1,3-benzothiadiazole via benzene-1,3,5-triyl branching centers. The obtained compounds have intense absorption in the wavelength range from 260 to 320 nm and effective blue-green luminescence with lifetime 6.0–7.4 ns. Spectral-luminescent studies of diluted solutions of new luminophores and model compounds in THF have shown that the main bands of their absorption spectra are formed as a result of transitions between overlapping molecular orbitals localized on various fragments of compounds **9** and **10**. Long wavelength bands are caused by transitions between the orbitals localized on the central fragments of compounds. Short wavelength bands are due to transitions between the orbitals localized on both central and peripheral fragments. Transitions between molecular orbitals localized on the fragment 4,7-diphenyl-2,1,3-benzothiadiazole are responsible for the fluorescence of compounds. The compounds

Table 1 Photophysical characteristics of new luminophores and model compounds in dilute THF solutions.^a

Compound	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon_{\text{max}} \times 10^{-4}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{PL}}/\text{nm}$	QY _{PL} (%)	τ/ns	k_r/ns^{-1}	k_{nr}/ns^{-1}
9	265	10.53	492	93	7.4	0.13	0.01
	387	1.50					
10	292	14.87	491	79	6.0	0.13	0.03
	385	1.42					
11^b	278	3.58	492	96	6.5	0.13	0.03
	385	1.39					
5	258	3.88	336	19	—	—	—
6	290	7.31	350	84	—	—	—

^a $\lambda_{\text{abs}}^{\text{max}}$ is wavelength of absorption maximum, ϵ_{max} is molar absorptivity, $\lambda_{\text{PL}}^{\text{max}}$ is wavelength of fluorescence maximum, QY_{PL} is fluorescence quantum yield, τ is fluorescence lifetime, k_r and k_{nr} are radiative and non-radiative constants, respectively. ^b Reported previously (ref. 14).

synthesized are promising for applications as wavelength-shifters in scintillators and optoelectronics.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.004.

References

- 1 K. R. J. Thomas, J. T. Lin, M. Velusamy, Y.-T. Tao and C.-H. Chuan, *Adv. Funct. Mater.*, 2004, **14**, 83.
- 2 J. Zhang, A. Kongsom, A. Sandberg, X. Wu, S. Nyström, U. Obermüller, B. M. Wegenast-Braun, P. Konradsson, M. Lindgren and P. Hammarström, *J. Med. Chem.*, 2019, **62**, 2038.
- 3 T. L. Mako, J. M. Racicot and M. Levine, *Chem. Rev.*, 2019, **119**, 322.
- 4 S. A. Ponomarenko, N. M. Surin, O. V. Borshchev, Y. N. Luponosov, D. Y. Akimov, I. S. Alexandrov, A. A. Burenkov, A. G. Kovalenko, V. N. Stekhanov, E. A. Kleymyuk, O. T. Gritsenko, G. V. Cherkaev, A. S. Kechek'yan, O. A. Serenko and A. M. Muzafarov, *Sci. Rep.*, 2014, **4**, 6549.
- 5 S. L. Lee and C.-J. Chang, *Polymers*, 2019, **11**, 206.
- 6 A. N. Chukhlantseva, M. V. Dmitriev, O. A. Maiorova, E. V. Shklyayeva and G. G. Abashev, *Mendeleev Commun.*, 2022, **32**, 268.
- 7 S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2000, **122**, 6335.
- 8 M. Villa, P. Ceroni and A. Fermi, *ChemPlusChem*, 2022, **87**, e202100558.
- 9 O. V. Borshchev, N. M. Surin, M. S. Skorotetcky and S. A. Ponomarenko, *INEOS OPEN*, 2019, **2**, 112.
- 10 S. A. Ponomarenko, N. M. Surin, M. S. Skorotetcky, O. V. Borshchev, S. A. Pisarev, E. A. Svidchenko, Y. V. Fedorov, F. Molins and T. Brixner, *J. Mater. Chem. C*, 2019, **7**, 14612.
- 11 F. Goubard and F. Dumur, *RSC Adv.*, 2015, **5**, 3521.
- 12 Z.-F. Chang, L.-M. Jing, C. Wei, Y.-P. Dong, Y.-C. Ye, Y. S. Zhao and J.-L. Wang, *Chem. – Eur. J.*, 2015, **21**, 8504.
- 13 Y. N. Luponosov, A. N. Solodukhin, D. O. Balakirev, N. M. Surin, E. A. Svidchenko, S. A. Pisarev, Y. V. Fedorov and S. A. Ponomarenko, *Dyes Pigm.*, 2020, **179**, 108397.
- 14 M. S. Skorotetcky, N. M. Surin, E. A. Svidchenko, S. A. Pisarev, Y. V. Fedorov, O. V. Borshchev, B. S. Kuleshov, P. A. Shaposhnik, O. A. Maloshitskaya and S. A. Ponomarenko, *J. Phys. Chem. B*, 2022, **126**, 10893.
- 15 P. S. Gribanov, D. A. Loginov, D. A. Lypenko, A. V. Dmitriev, S. D. Tokarev, A. E. Aleksandrov, A. R. Tameev, A. Yu. Chernyadyev and S. N. Osipov, *Mendeleev Commun.*, 2023, **33**, 701.
- 16 B. A. DaSilveira-Neto, A. S. Lopes, G. Ebeling, R. S. Gonçalves, V. E. U. Costa, F. H. Quina and J. Dupont, *Tetrahedron*, 2005, **61**, 10975.
- 17 N. S. Gudim, E. A. Knyazeva, L. V. Mikhalechenko, I. S. Golovanov, V. V. Popov, N. V. Obruchnikova and O. A. Rakitin, *Molecules*, 2021, **26**, 4931.
- 18 M. S. Skorotetcky, E. D. Krivtsova, O. V. Borshchev, N. M. Surin, E. A. Svidchenko, Y. V. Fedorov, S. A. Pisarev and S. A. Ponomarenko, *Dyes Pigm.*, 2018, **155**, 284.
- 19 A. G. Bonn, O. Yushchenko, E. Vauthey and O. S. Wenger, *Inorg. Chem.*, 2016, **55**, 2894.
- 20 M. S. Skorotetcky, O. V. Borshchev, G. V. Cherkaev and S. A. Ponomarenko, *Russ. J. Org. Chem.*, 2019, **55**, 25 (*Zh. Org. Khim.*, 2019, **55**, 40).
- 21 F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.
- 22 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
- 23 I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd edn., Academic Press, New York, 1971.

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