Synthesis of ferrocenylarylethylenes and their cyclodextrin complexes, which are potential materials for nonlinear optics

V. I. Sokolov and L. A. Bulygina*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085. E-mail: sokol@ineos.ac.ru

Cis- and *trans*-isomers of 1-ferrocenyl-2-(2-(4-)nitrophenyl)ethylenes and their complexes with β-cyclodextrin have been synthesized with the aim of studying their nonlinear optical properties.

Key words: 1-ferrocenyl-2-arylethylenes, cyclodextrin, complexes; nonlinear optics.

Nonlinear optical properties of substances are discovered by using highly intense light beams. It has become possible to observe them due to the invention of the laser. Interaction with an intense light beam can change molecular polarizability and the induced polarizability is expressed by the power series

$$P = \alpha E + \beta E^2 + \gamma E^3 + \ldots,$$

where E is the intensity of the electrical field.

The coefficients of the terms in which E is taken to powers greater than one characterize the second order (β), third order (γ), and higher order nonlinearity.[1] Second order nonlinear polarizability is also called *the first hyperpolarizability*. As E increases, the nonlinear effects rapidly become predominant. The second harmonic (in general, *n*th) is generated when an intense beam of light at frequency ν is passed through a substance with nonlinear optical properties. Under these conditions, light at a frequency of 2ν (in general, *n*ν) is formed. The frequency transformation occurs: an Nd-laser (ν 1.064 μm) emits light at 0.532 μm, which is half its frequency (the second harmonic). This allows one to obtain laser emission with multiple frequency magnitudes. The other area of the application of optical nonlinearity is connected to the practical aspects of the optical conversion, storage, and delivery of information.

A condition for the existence of the second harmonic, *i.e.*, a nonzero value of β, is the absence of a center of symmetry in the molecular crystal. The test most used for solid substances is the Kurts powder test[2] and urea is the standard. A reliable method for removing a center of symmetry from a molecule that is known to make it optically active is to sometimes include a "guest" molecule in the "host" matrix.

The search for new materials for nonlinear optics began in organometallic compounds some years ago.[1,3] As there are metallocene derivatives among already known groups of substances with large values of β, we decided to study them first. In the basic work (Ref. 4), it was shown that only the *cis*-isomer of 1-ferrocenyl-2-(*p*-nitrophenyl)ethylene, as distinct from the *trans*-isomer, had a nonzero β coefficient much exceeding the standard polarizability. Further, the enantiomeric 2-methylferrocenyl analog has been synthesized, in which a higher β value has been already found for the *trans*-isomer.

Another useful method of removing crystal center-symmetry is to obtain inclusion complexes. Thus, optical nonlinearity is observed even in the series of nonsubstituted metallocenes in channel type inclusion compounds with thiourea.[5] With the same purpose, but for organic compounds, cyclodextrin complexes have also been used.[6]

The main task of our research of the nonlinear optical properties of metallocenes was to study the influence of their inclusion in β-cyclodextrin on the value of the optical nonlinearity. With this purpose, the *cis-* and *trans*-isomers of 1-ferrocenyl-2-nitrophenylethylene (the *p*-isomer and the *o*-isomer, which has not before been described) were synthesized and their complexes with cyclodextrin were obtained. It was found that 2 equiv. of cyclodextrin are involved under these conditions, that is, both the ferrocenyl and aryl fragments are included.

The measurement of the optical nonlinearity by the Kurts powder method is at present under investigation.

In the near future we plan to obtain similar derivatives of ruthenocene and appropriate imines (Shiff's base).

Experimental

^{1}H NMR spectra were recorded on a Bruker-400HX instrument in $CDCl_3$; the internal standard was Me_4Si. UV spectra were recorded on a Specord UV-Vis spectrophotometer in hexane. Mass spectra were obtained on an MS-390 instrument.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 2361—2363, September, 1996.

1066-5285/96/4509-2243 $15.00 © 1997 Plenum Publishing Corporation

1-Ferrocenyl-2-(2-nitrophenyl)ethylene (1). Ferrocenylmethyl triphenylphosphonium iodide (3 g, 5.1 mmol) was added to Bu^{n}Li (10.2 mmol) in dehydrated ether (60 mL) in an argon atmosphere with stirring. The reaction mass was stirred for 3 h, and in that time the formation of (ferrocenylmethylene)triphenylphosphorane was quantitative. *o*-Nitrobenzaldehyde (1 g, 6.62 mmol) was added to the bright crimson-colored solution, and the reaction mass was stirred for 10 h, then the ether was replaced by dehydrated THF and the mixture was boiled for 2 h. The residue was filtered off, the solvent was evaporated, and the residue was chromatographed on an Al_2O_3 column (heptane as the eluent), which washed the *cis*- and *trans*-isomers off one after another. The yield of the *cis*-isomer was 28%, and the yield of the *trans*-isomer was 50%. Found (%): for the *cis*-isomer, C, 64.80; H, 4.78; N, 3.99; for the *trans*-isomer, C, 65.15; H, 4.47; N, 4.03. $C_{18}H_{15}NO_2Fe$. Calculated (%): C, 64.89; H, 4.54; N, 4.20. MS, *m/z*: 333 $[M]^+$. ^1H NMR, δ: *cis*-isomer, 4.1 (s, 5 H, $C_5\underline{H}_5$); 3.9, 4.14 (m, 4 H, $C_5\underline{H}_4$); 6.44 (d, 1 H, $Fc{-}CH{=}C\underline{H}$, J = 11.85 Hz); 6.68 (d, 1 H, $Fc{-}C\underline{H}$, J = 11.85 Hz); 7.5 (m, 3 H, H(Ar)); 8.1 (d, 1 H, H(Ar), J = 9.8 Hz); *trans*-isomer, 4.19 (s, 5 H, $C_5\underline{H}_5$); 4.38, 4.54 (m, 4 H, $C_5\underline{H}_4$); 6.92 (d, 1 H, $Fc{-}CH{=}C\underline{H}$, J = 15.8 Hz); 7.17 (d, 1 H, $Fc{-}C\underline{H}$, J = 15.8 Hz); 7.35 (m, 1 H, H(Ar)); 7.54 (m, 1 H, H(Ar)); 7.69 (d, 1 H, H(Ar), J = 7.76 Hz); 7.92 (d, 1 H, H(Ar), J = 7.7 Hz). UV, λ_{max}/nm: *cis*-isomer, 310, 420, and 469; *trans*-isomer, 226, 251, 274, and 488.

1-Ferrocenyl-2-(4-nitrophenyl)ethylene (2) was synthesized similarly to compound **1**. The yield of the *cis*-isomer was 30%, and that of the *trans*-isomer was 55%. Found (%): for the *cis*-isomer, C, 64.98; H, 4.69; N, 3.90; for the *trans*-isomer, C, 64.85; H, 4.83; N, 4.11. $C_{18}H_{15}NO_2Fe$. Calculated (%): C, 64.89; H, 4.54; N, 4.20. MS, *m/z*: 333 $[M]^+$. ^1H NMR, δ: *cis*-isomer, 4.12 (s, 5 H, $C_5\underline{H}_5$); 4.17, 4.24 (m, 4 H, $C_5\underline{H}_4$); 6.41 (d, 1 H, $Fc{-}CH{=}C\underline{H}$, J = 11.9 Hz); 6.52 (d, 1 H, $Fc{-}C\underline{H}$, J = 11.9 Hz); 7.49 (d, 2 H, H(2), H(6), J = 8.7 Hz); 8.13 (d, 2 H, H(3), H(5), J = 8.7 Hz); *trans*-isomer, 4.19 (s, 5 H, $C_5\underline{H}_5$); 4.41, 4.55 (m, 4 H, $C_5\underline{H}_4$); 6.7 (d, 1 H, $Fc{-}CH{=}C\underline{H}$, J = 15.75 Hz); 7.09 (d, 1 H, $Fc{-}C\underline{H}$, J = 15.75 Hz); 7.52 (d, 2 H, H(2), H(6), J = 8.7 Hz); 8.18 (d, 2 H, H(3), H(5), J = 8.7 Hz). UV, λ_{max}/nm: *cis*-isomer, 320, 406, and 466; *trans*-isomer, 350 and 485.

Complexes of 1 and 2 with β-cyclodextrin (1a and 2a). A solution of compound **1** (**2**) (a mixture of isomers) (0.1 g, 0.3 mmol) in benzene (3 mL) was gradually added to a warm solution of β-cyclodextrin (0.35 g, 0.3 mmol) in H_2O (15 mL). The mixture was stirred for 3 h at 60 °C, then the temperature was increased to 80 °C in order to evaporate the benzene, and the mixture was stirred for 4 h more at 60 °C. The mixture was cooled, and the pink precipitate that formed was filtered off, dried over P_2O_5, and washed with benzene and ether. The yield of complex **1a** was 38%; that of **2a** was 32%. Found (%): for **1a**, C, 45.53; H, 6.26; Fe, 1.84; for **2a**, C, 46.66; H, 6.41; N, 0.44. $C_{18}H_{15}FeNO_2 \cdot 2C_{42}H_{70}O_{35} \cdot 4H_2O$ (**1a**); $C_{18}H_{15}FeNO_2 \cdot 2C_{42}H_{70}O_{35} \cdot 2H_2O$ (**2a**). Calculated (%): for **1a**, C, 45.53; H, 6.26; Fe, 1.84; for **2a**, C, 46.42; H, 6.07; N, 0.53.

The authors wish to thank V. A. Tsyryapkin for help in the separation of *cis*- and *trans*-isomers **1** and **2** by liquid chromatography (on a Tsvet chromatograph).

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-33446a), INTAS (Grant 94 1716), as part of the "Supramolecular Chemistry CRG" Project (Grant 941435 CEE).

References

1. H. S. Nalwa, *Appl. Organomet. Chem.*, 1991, **5**, 349.
2. S. K. Kurtz, *J. Appl. Phys.*, 1968, **39**, 3798.
3. N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1994, **34**, 21.
4. M. L. H. Green, J. Qin, D. O'Hare, H. E. Bunting, M. E. Thompson, S. R. Marder, and K. Chatakondu, *Pure Appl. Chem.*, 1989, **61**, 817.
5. J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder, and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227.
6. S. Tomaru, S. Zembutsu, M. Kawachi, and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1984, 1207.
7. P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, **5**, 2990.

Received April 25, 1996