Synthesis and Structure of NLO-active 8,8-Dicyano-3-(4'-*N*,*N*-dimethylamino)phenylheptafulvene

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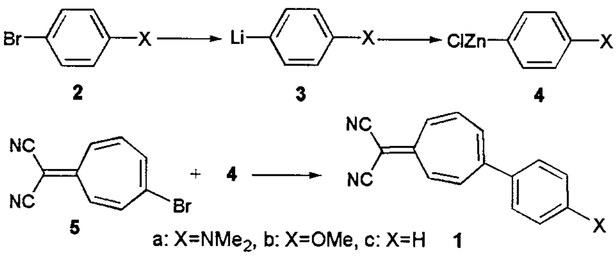
Some new 8,8-dicyanophenylheptafulvene derivatives have been synthesized, among which the title compound **1a** is found to crystallize in the polar space group of *P*1 showing non-linear optical characteristics. Compound **1a** is composed of a strong acceptor of the dicyanomethylene group and a strong donor of the dimethylamino group, both of which are combined with the π-conjugated phenylheptafulvene skeleton.

Stable, non-benzenoid compounds as characterized by large permanent dipole moments are frequently colored in spite of their small molecular weights. For example, non-benzenoid azulene has a brilliant blue color; whereas naphthalene, an isomer of azulene, is colorless.[1] We regard this kind of non-benzenoid systems as a potential chromophore and focus our attention on 8,8-dicyanoheptafulvene.

As is well known, the π-conjugated system such as benzene, biphenyl and azo dyes exhibits a high second-order hyperpolarizability of the molecule (*β*) when donor and acceptor substituents are introduced into both sides of the π-conjugated skeleton.[2] Our non-benzenoid system based on phenylheptafulvene derivatives has a similar structure and is composed of a variety of strong donor and acceptor as shown in our previous reports.[3,4] In the course of our studies on the synthesis and electronic applications of phenylheptafulvenes, we found that 8,8-dicyano-3-(4'-*N*,*N*-dimethylamino)phenyheptafulvene **1a** crystallizes in the polar space group of *P*1 showing non-linear optical (NLO) properties.[5] The present paper reports mainly on the synthesis of the title compound.

The synthetic procedure for phenylheptafulvenes **1a-c**[6] is outlined in Scheme 1. The key step of the present synthesis is the reaction between compounds **4** and **5** and was achieved, with high yield, by means of the palladium-catalyzed cross-coupling employed originally for the preparation of unsymmetrical biaryls.[7] The present procedure was found to be very effective in preparing non-benzenoid chromophore such as **1**, featuring high chemo- and regioselectivity as well as high cross-coupling ratios. The reaction proceeds in the following way. To a solution of 4-*N*,*N*-dimethylaminophenyl-lithium **3a**, prepared by reaction of 2.00 g (10 mmol) of 4-bromo-*N*,*N*-dimethylaniline **2a** in 10 ml of THF and 13.0 ml (22 mmol) of 1.7 M *tert*-butyllithium in pentane at −72 °C under argon, was added a solution of 2.00 g (15 mmol) of zinc chloride in 20 ml of THF. The Pd(0) catalyst was prepared by treating 0.56 g (0.8 mmol) of $Cl_2Pd(PPh_3)_2$ dissolved in 5 ml of THF with 1.1 ml (1.6 mmol) of 1.5 M diisobutylaluminium hydride in toluene. To this catalyst were added 2.05 g of 3-bromo-8,8-dicyanoheptafulvene **5**[8] in 10 ml of THF and the arylzinc chloride **4a** prepared above. The reaction mixture was stirred for 4 h at room temperature. After quenching with aqueous HCl and usual work-up, chromatography on silica gel eluting with benzene/ether (10:1) gave the cross-coupling product **1a** in 76% yield as deep violet needles (mp 223-224 °C). Similarly, 8,8-dicyano-3-(4'-methoxy)phenylheptafulvene **1b** and 8,8-dicyano-3-phenylheptafulvene **1c** were prepared as orange red needles (mp 199-200 °C) in 85% yield and orange needles (mp 182-183 °C) in 68% yield, respectively.



Scheme 1.

Figure 1 shows the UV-VIS spectra of phenylheputafulvene derivatives **1a-c** and 8,8-dicyanoheptafulvene **6** in 1,4-dioxane.

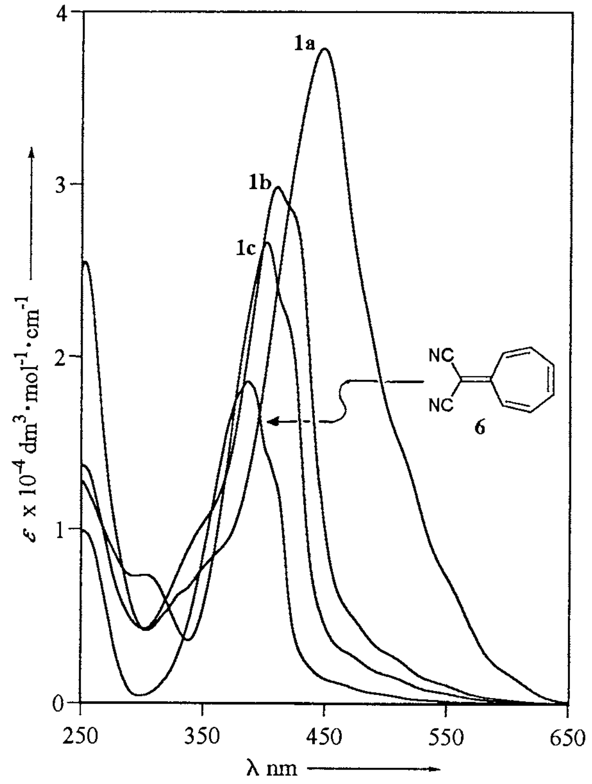


Figure 1. UV-VIS spectra for compounds **1a**, **1b**, **1c**, and **6**.

These compounds exhibit exactly the same spectral shape. However, the absorption maximum appears at longer wavelengths in the order of **6**, **1b**-**c** and **1a** due to π-electron delocalization, accompanied by an increase in absorption intensity. In particular, the -NMe_2 group (strong donor) in **1a** is quite effective in displacing the absorption maximum towards longer wavelengths as compared with that of -OMe in **1b** and -H in **1c**.

Figure 2 shows the projection the crystal structure of **1a** onto the (a,b) plane.[9] The seven-membered ring and the phenyl ring are twisted in opposite directions ("propeller type"). Furthermore, the torsion angles are different for each molecule in the unit cell: 34.1°, 30.4°, 34.4°, and 29.0° for molecules A, B, C, and D, respectively. Two molecules are paired up, due to the large dipole moment of **1a** (10.2 D as calculated by MOPAC 93),[10] to form a dimer-like structure (molecules A & B and molecules C & D) so as to reduce the electrostatic energy.

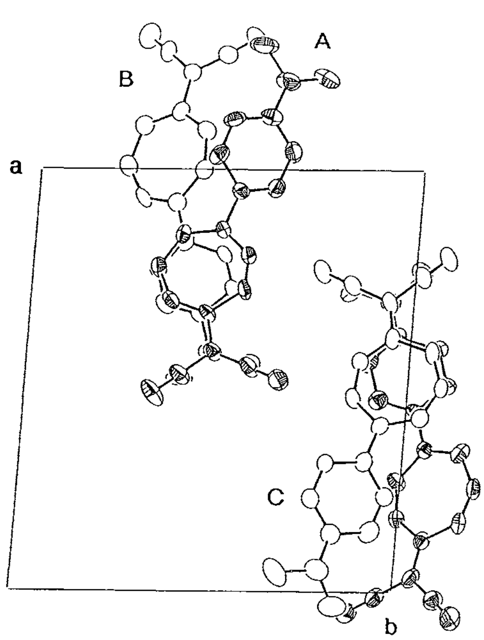


Figure 2. Projection of the crystal structure of compound **1a** on the (a, b) plane.

The NLO characteristic of compound **1a** was evaluated by a method based on the electro-optic coefficient.[11,12] The thin film of polymethylmethacrylate containing **1a** in 6.9 w/w% gave a $\mu\beta$ value of about $1.2\text{x}10^{-45}$ esu, where μ and β denote the dipole moment and the second-order hyperpolarizability of the molecule, respectively. This is approximately 1.5 times larger than that of Disperse Red 1.[13]

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References and Notes

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6 Spectral data for compounds **1a**, **1b**, and **1c** are follows: **1a**: IR (KBr), ν_{max}/cm^{-1} 2200 (C≡N); ^1H-NMR ($CDCl_3$, 270 MHz), δ 3.06 (s, 6H, -NMe_2), 6.74 (d, J= 9.1 Hz, 2H), 7.02 (m, 2H), 7.23 (ddd, J= 10.6, 2.0 and 2.0 Hz, 1H), 7.36 (dd, J= 11.9 and 2.0 Hz, 1H), 7.40 (d, J= 9.1 Hz, 2H), 7.43 (dd, J= 11.9 and 2.0 Hz, 1H), ^{13}C-NMR ($CDCl_3$, 67.5 MHz), δ 40.11 (-NMe_2), 66.31, 112.22, 115.45, 115.54, 126.88, 128.36, 131.64, 132.24, 134.59, 138.96, 140.25, 151.32, 162.59, High MS; Found: M^+, 273.1224, $C_{18}H_{15}N_3$ requires M, 273.1182. **1b**: IR (KBr), ν_{max}/cm^{-1} 2150 (C≡N); ^1H-NMR ($CDCl_3$, 270 MHz), δ 3.87 (s, 3H, -OMe), 6.99 (d, J= 9.0 Hz, 2H), 7.02 (m, 2H), 7.29 (d, J= 12.1 Hz, 1H), 7.30 (d, J= 13.2 Hz, 1H), 7.43 (d, J= 9.0 Hz, 2H), 7.44 (dd, J= 12.1 and 2.0 Hz, 1H), ^{13}C-NMR ($CDCl_3$, 67.5 MHz), δ 55.46 (-OMe), 68.06, 114.68, 114.88, 114.95, 128.55, 128.36, 132.67, 132.97, 134.03, 134.70, 138.58, 140.43, 150.69, 161.02, High MS; Found: M^+, 260.0943, $C_{17}H_{12}N_2O$ requires M, 260.0951. **1c**: IR (KBr), ν_{max}/cm^{-1} 2230 (C≡N); ^1H-NMR ($CDCl_3$, 270 MHz), δ 7.04 (dd, J= 11.8 and 8.3 Hz, 1H), 7.06 (dd, J= 11.8 and 2.0 Hz, 1H), 7.35 (d, J= 12.1 Hz, 1H), 7.36 (d, J= 8.3 and 2.0 Hz, 1H) 7.44 (d, J= 12.1 Hz, 1H), 7.47 (s, 5H, -Ph), ^{13}C-NMR ($CDCl_3$, 67.5 MHz), δ 69.24, 114.70, 114.74, 127.04, 129.22, 129.65, 133.71, 134.81, 135.24, 138.44, 140.47, 140.56, 151.00, 162.62, High MS; Found: M^+, 230.0880, $C_{16}H_{10}N_2$ requires M, 230.0918.

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9 Crystallographic data for **1a** (black prisms, recrystallized from THF): $C_{18}H_{15}N_3$, M_r 273.3, triclinic, space group $P1$, a= 13.091 Å, b= 14.417 Å, c= 7.790 Å, α= 97.81°, β= 93.48°, γ= 85.88°, V= 1454.6 $Å^3$, Z= 4, D_x= 1.25 $g{\bullet}cm^{-3}$, R= 0.0055, R_w= 0.0073, 4970 unique reflections with $I > 1.0\sigma\ (I)$.

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13 Disperse Red 1 (DR1) is an NLO-active, commercial dyestuff. ($\mu\beta$ product: about $0.8\text{x}10^{-45}$ esu).