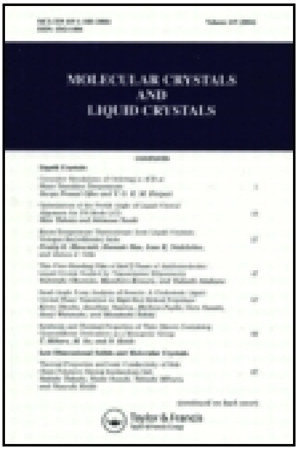

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A Novel NLO-Active, Non-Benzenoid Compound Based on 8, 8-Dicyano-3-(4′-dimethylamino)-phenylheptafulvene-Crystal and Electronic Structures -

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A Novel NLO-active, Non-benzenoid Compound Based on 8,8-Dicyano-3-(4'-dimethylamino)-phenylheptafulvene

- Crystal and Electronic Structures -

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Some new 8,8-dicyanoheptafulvene derivatives have been synthesized, among which the title compound (**1a**) is found to crystallize in a polar space group of $P1$ showing nlo-characteristics. The molecule is composed of a strong acceptor of the dicyanomethylidene group and a strong donor of the dimethylamino group, both of which are combined with the π-conjugated heptafulvene skeleton. Compound **1a** is therefore typical of an intramolecular CT compound, for which high second-order hyperpolarizability is expected. For this reason, electronic structure has been investigated in solution and in the solid state on the basis of the molecular and crystal structures together with molecular orbital calculations. The solid-state spectrum is found to be strikingly different from the solution spectrum because of the extent of conjugation between the seven-membered ring and the phenyl ring. There are two electronic transitions A (about 450 nm) and B (580-650 nm) in the solid. Band A is due mainly to the 8,8-dicyanoheptafulvene skeleton while band B is of charge-transfer character due to the dicyanomethylidene and dimethylamino groups.

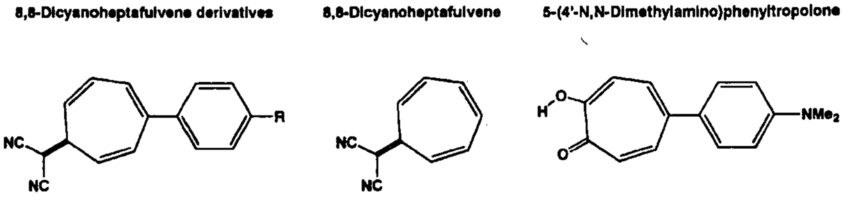
Keywords: heptafulvene; non-benzenoid; NLO; crystal structure; electronic structure; MO calculation

INTRODUCTION

Stable, non-benzenoid compounds, characterized by large dipole moments, are frequently colored in spite of their small molecular weights. For example, non-benzenoid azulene bears a brilliant color of blue; whereas naphthalene, an isomer of azulene, is colorless[1]. We regard this kind of non-benzenoid system as a potential chromophore and focus our attention on 8,8-dicyanoheptafulvene derivatives[2-4].

In our recent investigation[5], an attempt has been made to synthesize a series of 8,8-dicyano-3-phenylheptafulvene derivatives (**1a**-**1d**) as shown in Fig.1 in order to explore nlo-active compounds. Among these, compound **1a** was found to give an intense absorption band in the visible region and to crystallize in a polar space group of *P*1 characterized by non-centrosymmetry[6]. This compound gave an $\mu\beta$ product of about 1.2×10^{-45} esu and was claimed for nlo characteristics[7], where μ and β denote the dipole moment and the second-order hyperpolarizability of the molecule, respectively.

The purpose of the present investigation is to characterize the electronic structure of compound **1a** in solution and in the solid state on the basis of molecular and crystal structures.



1a $R=NMe_2$ **1b** $R=OMe$ **2** **3**
1c $R=OH$ **1d** $R=H$

FIGURE 1 8,8-Dicyanoheptafulvene derivatives and related compounds.

RESULTS AND DISCUSSION

Solution spectra

Fig.2 shows the solution spectra in benzene for compounds **1a**, **1d** and **3**. The spectral shape of compounds **1b** (λ_{max}=412 nm; $\varepsilon=2.5\times10^4$ cm^{-1}), **1c** (λ_{max}=411 nm; $\varepsilon=2.8\times10^4$ cm^{-1}) and **2** (λ_{max}=350 nm; $\varepsilon=2.2\times10^4$ cm^{-1}) is exactly the same as that of compound **1d** and these spectra are omitted for clarity. The absorption spectra for compounds **1a** and **1d** are characterized by a couple of small absorption shoulders (as indicated by arrows) in the longer-wavelength region and these are equally spaced with an interval of about 1390 cm^{-1}. Since the present fine structure is also observed in compounds **1b**, **1c** and **2** and is not observed in compound **3**, this is clearly related to the skeleton of 8,8-dicyanoheptafulvene (compound **2**).

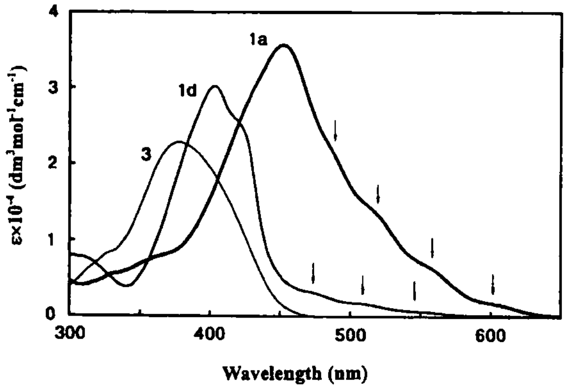


FIGURE 2 Solution spectra in benzene for compounds **1a**, **1d** and **3**.

While the absorption maxima of compounds **1b**, **1c** and **1d** appear around 410 nm, compound **1a** alone exhibits an absorption maximum at a longer wavelength of about 460 nm. This indicates that the electrodonating ability of the –NMe_2 group is significantly larger than that of the others. On the other hand, the absorption maximum of compound **3** appears at a much shorter wavelength of around 350 nm as compared with that of compound **1a**. This is clearly due to the difference in electroaccepting power of tropolone and 8,8-dicyanoheptafulvene.

Crystal structure of compounds 1a and 3

The single crystals of compounds **1a** and **3** were grown by recrystallization from solution in THF (tetrahydrofuran). The crystallographic data for compounds **1a** and **3** is given in Table 1[6]. Compound **1a** belongs to a polar space group of *P*1 and is therefore nlo-active, while compound **3** to *C*2/c.

TABLE 1 Crystallographic data for compounds **1a** and **3**

	Compound 1a	Compound 3
Formula	$C_{17}H_{15}N_3$	$C_{15}H_{15}O_2N$
Crystal system	triclinic	monoclinic
Space group	*P*1	*C*2/c
Molecular weight	273.3	241.3
Z	4	8
Moleclar symmetry	C_1	C_1
Torsion angle (°)*	32**	40
a (Å)	13.091	25.237
b (Å)	14.417	7.312
c (Å)	7.79	13.895
α (°)	97.81	90
β (°)	93.48	105.9
γ (°)	85.88	90
Volume (Å³)	1454.6	2466.0
Density (g/cm³)	1.25	1.30
Color	black	pale yellow

* The torsion angle between the seven-membered ring and the phenyl ring.

** The angle is different for each molecule in the unit cell. So the averaged value is given here.

Fig.3 shows the projection of the crystal structure of compound **1a** onto the (*a*,*b*) plane, where molecules 1, 2, 3 and 4 correspond to those in Table 2. Because of the large dipole moment, two molecules are paired up to form a dimeric structure in order to reduce the electrostatic energy. However, it should be noted that the two molecules are not connected by a center of symmetry, because the torsion angle for each molecule is slightly different.

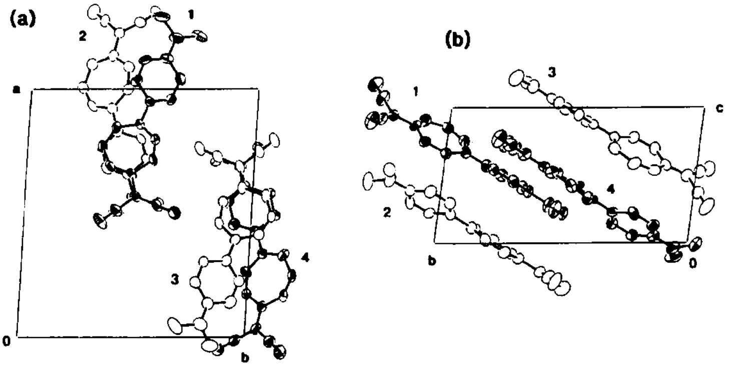


FIGURE 3 Projection of the crystal structure of compound **1a** onto: (a) (a,b) plane and (b) (b,c) plane.

TABLE 2 Conformation of four molecules in the unit cell and their calculated absorption bands

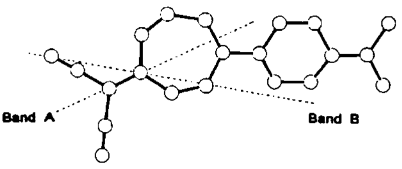
Molecules	Dipole moment** (*D*)	Torsion angle*** (°)	Band A (HOMO/2ndLUMO)		Band B (HOMO/LUMO)	
			λ (nm)	*f*****	λ (nm)	*f*****
1	10.2	-34.1	404.0	1.082	456.1	0.218
2	10.2	30.4	395.0	1.085	455.4	0.194
3	9.5	34.4	367.9	1.027	427.0	0.157
4	10.7	-29.0	394.3	1.084	461.9	0.236

* Calculated by ZINDO[illegible]

** Calculated by MOPAC93[illegible]

*** Positive or negative symbol denotes the direction of the torsion angle.

****Oscillator strength



Calculated absorption bands of compound 1a

Table 2 shows the dipole moment and torsion angle for molecules 1, 2, 3 and 4 of compound **1a** in the unit cell together with calculated absorption bands in the visible region, using the x,y,z coordinate sets of the X-ray structure[6]. It is remarkable to note that the torsion angle is greatly reduced (32° on the average) as compared with that in solution (46.8°[5]). The direction of the transition moments for absorption bands A and B is also illustrated by dotted line in the inset. Band A is the HOMO/2ndLUMO transition while band B the HOMO/LUMO.

Polarized reflection spectra of compound 1a

Fig.4(a) shows the polarized reflection spectra measured on the (100) plane of single crystals of compound **1a** by means of a microscope-spectrophotometer (see Fig.3(b)). In the visible region, there are three intense reflection bands for polarization perpendicular to the *c*-axis. On the other hand, the intensities of these bands are greatly diminished for polarization parallel to the *c*-axis. These solid-state spectra are strikingly different from solution spectra shown in Fig.2.

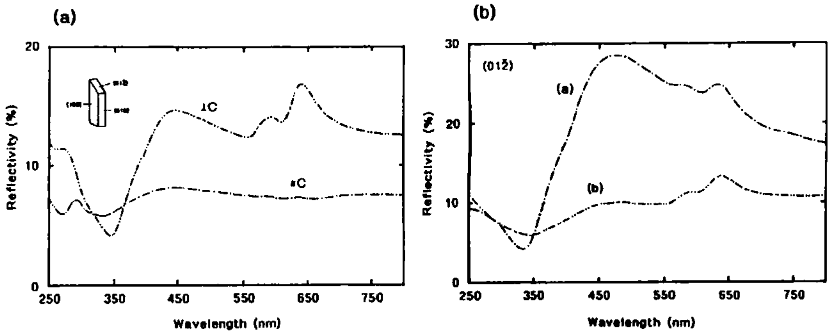


FIGURE 4 Polarized reflection spectra of compound **1a**:
(a) measured on the (100) plane and (b) measured on the (01-2) plane.

The present reflection bands are assigned, as follows, by considering the polarization direction as well as the direction of the transition moments. As shown in the inset of Table 2, the transition moments for bands A and B lie on the molecular plane. Excitation with polarized light perpendicular to the *c*-axis (Fig.3(b)) causes both reflection bands A and B to appear in the visible region; whereas the polarization parallel to the *c*-axis is quite ineffective for the excitation, because it intersects the transition moment at an angle of about 65°.

In order to separate bands A and B, further experiments were performed on the (01-2) plane, where the molecular arrangement is nearly given by Fig.3(a). Two polarization directions were selected as follows: (a) one is with an angle of 45° from the *b*-axis towards the *a*-axis in an attempt to excite band A more predominantly than band B, and (b) the other is with an angle of 45° towards the negative direction of the *a*-axis in order to excite band B more significantly than band A. The result is given in Fig.4(b). The two reflection bands at longer wavelengths move or behave in the same manner for both polarizations. This indicates that these bands are attributed to one electronic transition (namely, band B) and that the band at 637 nm is assigned to the 0-0 transition and the band at 585 nm is the (0-1) vibronic band, in which the vibrational mode of about 1390 cm^{-1} is coupled with the pure electronic band.

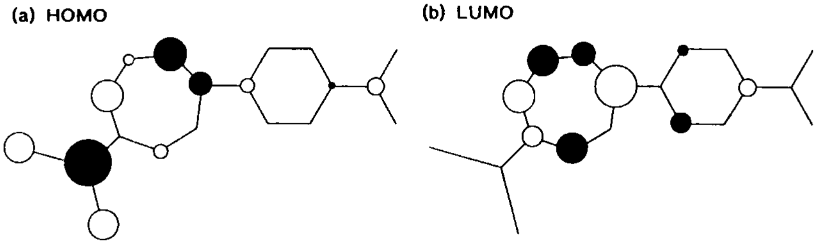


FIGURE 5 HOMO and LUMO diagrams for compound **1a** in the solid state. The open and closed circles denote the positive and negative sign of the coefficient of the molecular orbital. The size of each circle is proportional to the MO coefficient.

Band B (HOMO/LUMO transition) appears only in the solid state due to the reduction in torsion angle on going from solution to the solid state. The HOMO/LUMO diagrams shown in Fig.5 give a clear picture about the nature of the present electronic transition. In the ground state (HOMO), the electrons are localized mainly in the 8,8-dicyanoheptafulvene skeleton and partly in the dimethylamino group. On the other hand, in the excited state (LUMO), the electron is mainly distributed on the seven-membered ring and partly on the phenyl ring, showing a charge-transfer character.

CONCLUSIONS

The $-NMe_2$ group is found to be, by far, an effective donor as compared with the others: $-OMe$, $-OH$ and $-H$. In the solid state, the torsion angle in compound **1a** is significantly reduced (46.8→32.0°) due to the strong electrodonating ability of the $-NMe_2$ group as well as intermolecular interactions. This facilitates the electron jump in the excited state to give an intense absorption band around 640 nm; whereas the band around 450 nm is, for the most part, characterized by the transition in the 8,8-dicyanoheptafulvene skeleton.

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