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Spectral and Conformational Change on Deprotonation in 8,8-Dicyano-3-(4′-hydroxy)phenylheptafulvenes

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ABSTRACT

Some new 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvenes, non-benzenoid chromophoric compounds, have been synthesized and their electronic spectra have been investigated in solution with special attention to the spectral and conformational change on deprotonation. A large bathochromic shift from 434 to 643 nm (about 209 nm; about 7489 cm^{-1}*) has been observed on deprotonation in dimethylsulfoxide, accompanied by a change in molecular conformation. Molecular orbital calculations revealed that the torsion angle between the seven-membered ring and the phenyl ring amounts to about 45–52° in the initial state; whereas the torsion angle is greatly reduced by about 20° due to deprotonation, which results in a larger overlapping of* π *orbitals between the two rings. A significant change in chemical shifts in the* ^{13}C*-NMR spectra has also been observed on deprotonation, indicating that the deprotonation effect (*$-O^-$*) at the oxygen atom is well propagated throughout the chromophore, and the electrons are then delocalized. The computed optical absorption spectra are qualitatively in good agreement with experimental determination. The large bathochromic displacement on deprotonation can be interpreted in terms of the increased electron density in the chromophore, accompanied by the conjugation enhancement between the seven-membered ring and the phenyl ring.*
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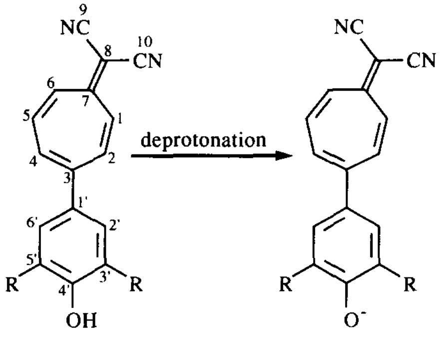
Keywords: non-benzenoid chromophore, 8,8-dicyanoheptafulvene, electronic spectra, deprotonation, bathochromic shift, MO calculations.

1 INTRODUCTION

Azulene, ferrocene and tropolone are the typical examples of non-benzenoid compounds which possess pronounced aromatic character [1]. Azulene, for example, may be regarded as a compound which contains a tropylium cation fused to a cyclopentadienide ion, forming a stable ten π-electron system (Hückel's rule) characterized by a relatively large dipole moment. Although azulene is an isomer of the colorless naphthalene, it is highly colored and has therefore attracted attention as a chromophore for pigmentary and electronic applications [2–5]. In particular, azulenium salts are of practical interest because of their high photoconductivity in the near-IR region and have been reported as being useful as electrophotographic photoreceptors for laser printers based on GaAsAl laser diodes [2].

8,8-Dicyanoheptafulvene, the most stable heptafulvene, is another example which exhibits aromatic character. Aromaticity is achieved by introducing a dicyano group (a strong electron-acceptor), which draws enough of the π-electron density of the seven-membered ring to itself to form a stable six π-electron system [6]. This compound is again characterized by an extremely large dipole moment (7.49 *D*) [7].

Most aromatic molecules have an inversion center (C_i) showing no dipole moments, whereas non-benzenoid aromatic compounds such as azulene, tropolone and dicyanoheptafulvene, are characteristic of polar molecules. We believe that the polar molecules may have different intermolecular interactions compared with nonpolar molecules, and thus different molecular arrangements in the solid state. Therefore, we expect in these compounds some novel optical properties to appear, such as those of high photocon-



1a; R = H
b; R = Me
c; R = *tert*-Bu

Scheme 1 Deprotonation by means of a base.

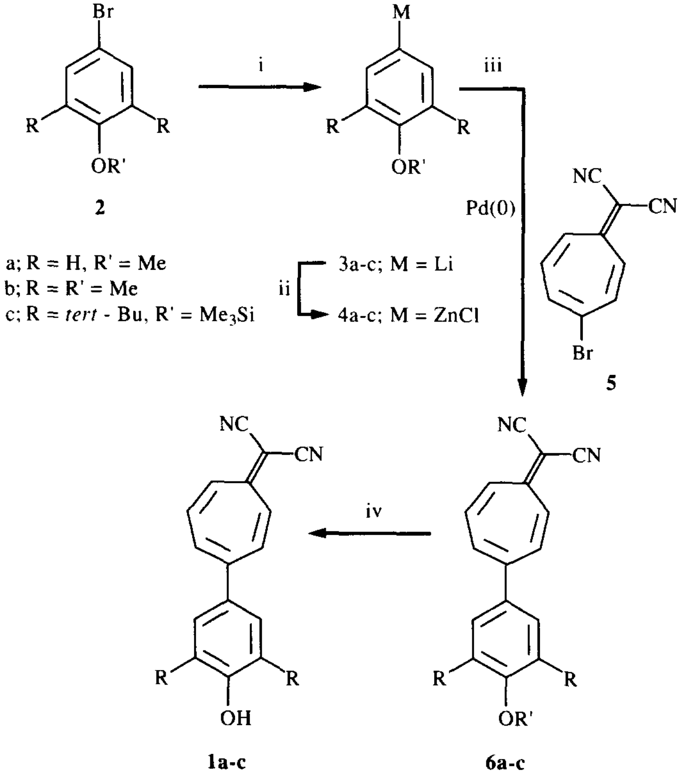
ductivity as shown by azulenium salts [2]. For this reason, we have now synthesized 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvene (Scheme 1) together with its deprotonated form, in an attempt to extend the chromophore and to achieve an intense optical absorption in the visible region for electronic applications.

We report here the electronic spectra of 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvene in solution and discuss the spectral and conformational change on deprotonation in terms of molecular orbital (MO) calculations and ^{13}C-NMR spectra.

2 EXPERIMENTAL

2.1 Synthesis

The synthetic procedure for 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvenes **1a-c** is outlined in Scheme 2. The Pd(0)-catalyzed cross-coupling reaction has



Scheme 2 *Reagents and conditions*: i, 2.0*eq* Bu^tLi/THF, −72°C; ii, 1.2*eq* $ZnCl_2$; iii, 10 mol% $Cl_2Pd(PPh_3)_2$-DIBAL-H, 12h, room temp.; iv, 3.5*eq* BBr_3/CH_2Cl_2, room temp. for 6a-b, and 6 mol dm-3 HCl for 6c (Overall yield based on 5; 1a: 71%, 1b: 61%, 1c: 66%)

been widely used [8] for the synthesis of the methoxy derivatives **6a-b** and trimethylsilyloxy derivative **6c**, and these are the precursors of the heptafulvenes **1a-c**. 4-Methoxyphenylzinc chloride **4a**, derived from interaction of 4-methoxyphenyllithium **3a** with zinc chloride, reacted readily with 3-bromo-8,8-dicyanoheptafulvene **5** [9] in the presence of 10 mol% of the Pd(0)-catalyst prepared *in situ* by reduction of $Cl_2Pd(PPh_3)_2$ with diisobutylaluminium hydride (DIBAL-H) to give **6a** in 85% yield. Demethylation of **6a** with boron tribromide (BBr_3) gave the heptafulvene **1a** in 84% yield as orange red crystals.

Similarly, the dimethyl derivative **1b** was prepared as orange red crystals using 2,6-dimethyl-4-bromoanisole **2b** as an arylbromide and the overall yield, based on **5**, was 61%. The di-*tert*-butyl derivative **1c** was also synthesized in a similar way, while the hydroxyl group was protected as the trimethylsilylether. The bromide **2c** gave **6c** in excellent yield. Compound **6c** was readily desilylated with 6 mol dm^{-3} of HCl in aqueous tetrahydrofuran (THF) to give **1c** as dark red crystals in 66% overall yield.

Details on the synthesis of compounds **1a-c** together with their characterisation are given below:

4-Methoxyphenylzinc chloride

A 1.7 mol dm^{-3} solution of *tert*-butyllithium in pentane (7.0 cm^{-3}, 12.0 mmol) was added dropwise, at −72°C under argon, to a solution of 4-bromoanisole (1.12 g, 6.0 mmol) in dry THF (6 cm^{-3}). After 1 h at −72°C, to the resulting solution was added a solution of anhydrous zinc chloride (1.14 g, 8.4 mmol) in dry THF (10 cm^{-3}). The mixture was further stirred at −72°C for 30 min and then at room temperature (rt) for 1 h, giving 4-methoxyphenylzinc chloride **4a**.

8,8-Dicyano-3-(4′-methoxy)phenylheptafulvene

A solution of 3-bromo-8,8-dicyanoheptafulvene **5** (0.93 g, 3.6 mmol) in dry THF (20 dm^{-3}) was added to Pd(0) catalyst prepared by reduction of $Cl_2Pd(PPh_3)_2$ (0.28 g, 0.4 mmol) in dry THF (2 cm^{-3}) with 1.5 mol dm^{-3} of DIBAL-H in toluene (0.5 cm^{-3}, 0.8 mmol), followed by an addition of a THF solution of **4a**. After 3 h at rt, the solution was poured into cold 1 mol dm^{-3} HCl and extracted with ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate and water, and dried. Chromatography on silica gel, eluting with benzene/ethyl ether (100:2), gave 8,8-dicyano-3-(4′-methoxy)phenylheptafulvene **6a**. The product was then recrystallized twice from dichloromethane (CH_2Cl_2)/hexane. Yield 85%. Orange red needles; mp 199–200°C (Found: M^+, 260.094. $C_{17}H_{12}N_2O$ requires *M*,260.095; ν_{max}/cm^{-1} 2150 (C≡N); δ_H ($CDCl_3$) 3.87 (s, 3H, -OCH_3), 6.99 (d, 2H,*J* 9, 3′- and 5′-H), 7.02 (m, 2H, 4- and 5-H), 7.29 (d, 1H,*J* 12, 1-H), 7.30 (d, 1H, *J* 13, 6-H), 7.43 (d, 2H, *J* 9, 2′- and 6′-H), 7.44 (dd, 1H, *J* 12 and 2, 2-H), δ_{C} ($\mathrm{CDCl_3}$) 55.46 (-OCH3), 68.05 (8-C), 114.68 (3′- and 5′-C), 114.88, 114.95 (each 9-, 10-C), 128.55 (2′- and 6′-C), 132.67 (1′-C), 132.97 (4-C), 134.03 (1-C), 134.70 (6-C), 138.58 (2-C), 140.43 (5-C), 150.69 (3-C), 161.02 (4′-C), 162.60 (7-C); *m*/*z* 260 ($\mathrm{M^+}$, base peak).

Demethylation of ***6a***

A 1.0 mol dm^{-3} solution of $\mathrm{BBr_3}$ in $\mathrm{CH_2Cl_2}$ (6.3 cm^{-3}, 6.3 mmol) was added dropwise, at rt under argon, to a solution of 8,8-dicyano-3-(4′-methoxy)-phenylheptafulvene **6a** (0.51 g, 2.0 mmol) in dry $\mathrm{CH_2Cl_2}$ (50 cm^{-3}). After 12 h at rt, the solution was poured into cold water and extracted with $\mathrm{CH_2Cl_2}$. After usual work-up, chromatography on silica gel eluting with benzene/ethyl ether (10:1) gave 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvene **1a**. The product was then recrystallized twice from $\mathrm{CH_2Cl_2}$/ethanol. Yield 84%. Orange red needles; mp 250–252°C (Found: $\mathrm{M^+}$, 246.0804. $\mathrm{C_{16}H_{10}N_2O}$ requires *M*, 246.0793); ν_{max}/cm^{-1} 2215 (C≡N); δ_{H} (DMSO-$\mathrm{d_6}$) 6.99 (d, 2H, *J*9, 3′- and 5′-H), 7.02 (m, 2H, 4- and 5-H), 7.29 (d, 1H, *J*12, 1-H), 7.30 (d, 1H, *J*13, 6-H), 7.43 (d, 2H, *J*9, 2′- and 6′-H), 7.77 (dd, 1H, *J*12 and 2, 2-H), 10.08 (br s, 1H, -OH), Table 1 lists the complete signal assignments (δc) in DMSO-$\mathrm{d_6}$; *m*/*z* 247 ($\mathrm{M^+}$ + 1, 35%), 246 ($\mathrm{M^+}$ base peak).

8,8-Dicyano-3-(3′-5′-dimethyl-4′-methoxy)phenylheptafulvene

Yield 80%. Orange red needles; mp 228–229°C ($\mathrm{CH_2Cl_2}$/hexane) (Found: $\mathrm{M^+}$, 280.1300. $\mathrm{C_{19}H_{16}N_2O}$ requires *M*, 288.1262); ν_{max}/cm^{-1} 2215 (C≡N); δ_{H} ($\mathrm{CDCl_3}$) 2.34 (s, 6H, -$\mathrm{CH_3}$), 3.77 (s, 3H, -$\mathrm{OCH_3}$), 7.04 (m, 2H, 4- and 5-H), 7.12 (s, 2H, 2′- and 6′-H), 7.28 (d, 1H, *J*12, 1-H), 7.43 (d, 1H, *J*12, 6-H), 7.45 (dd, 1H, *J*12 and 3, 2-H), δ_{C} ($\mathrm{CDCl_3}$) 16.25 (-$\mathrm{CH_3}$), 59.79 (-$\mathrm{OCH_3}$), 68.99 (8-C), 114.84, 114.90(each 9-, 10-C), 127.71 (2′-and 6′-C), 133.23 (3′- and 5′-C), 133.23 (4-C), 134.59 (1- and 6-C), 135.85 (4′-C), 138.53 (2-C), 140.63 (5-C), 158.49 4′-C), 162.64(7-C); *m*/*z* 290 ($\mathrm{M^+}$ + 1, 30%), 289 ($\mathrm{M^+}$, base peak).

8,8-Dicyano-3-(3′,5′-dimethyl-4′-hydroxy)phenylheptafulvene

Yield 76%. Orange red needles; mp >270°C (THF-ethanol) (Found: $\mathrm{M^+}$, 274.1148. $\mathrm{C_{18}H_{14}N_2O}$ requires *M*, 274.1116); ν_{max}/cm^{-1} 2220 (C≡N); δ_{H} (DMSO-$\mathrm{d_6}$) 2.28 (s, 6H, -$\mathrm{CH_3}$), 7.35 (s, 2H, 2′ and 6′H), 7.41 (m, 2H, 4- and 5-H), 7.53 (d, 1H, *J* 13, 1-H), 7.63 (d, 1H, *J*12, 6-H), 7.88 (dd, 1H, *J*13 and 2, 2-H), 8.88 (br s, 1H, -OH), δ_{C} (DMSO-$\mathrm{d_6}$) 16.75 (-$\mathrm{CH_3}$), 63.98 (8-C), 115.69 (9- and 10-C), 124.98 (3′- and 5′-C), 127.76 (2′- and 6′-C), 130.35 (1′-C), 132.11 (4-C) 134.20 (1-C), 134.50 (6-C), 140.72 (2-C), 141.80 (5-C) 150.89 (3-C), 155.51 (4′-C), 162.62 (7-C); *m*/*z* 275 ($\mathrm{M^+}$ + 1, 23%), 274 ($\mathrm{M^+}$, base peak).

*8,8-Dicyano-3-(2',5'-di-*tert*-butyl-4'-methoxy)phenylheptafulvene*
In a similar manner described for **6a**, a solution of 3,5-di-*tert*-butyl-4-trimethylsilyloxyphenylzinc chloride **4c** (6.0 mmol) in dry THF (20 dm^{-3}) was treated with a solution of **5** (1.00 g, 3.9 mmol) in the presence of the Pd(0) catalyst. After 3 h at rt, the solution was poured into cold 6 mol dm^{-3} HCl (20 cm^{-3}) while stirring at rt for 3 h and then extracted with ethyl acetate. 8,8-Dicyano-3-(2',5'-di-*tert*-butyl-4'-hydroxy)phenylheptafulvene **1c** was isolated as dark red needles. The product was then purified by chromatography on silica gel, eluting with benzene/ethyl ether (10:1), and finally recrystallized from CH_2Cl_2/ethanol. Overall yield 66% based on 3-bromo-8, 8-dicyanoheptafulvene **5**. mp 255-256°C (Found: M^+, 358.2029. $C_{24}H_{26}N_2O$ requires 358.2045); ν_{max}/cm^{-1} 2215 (C≡N); δ_H (DMSO-d_6) 1.41 (s, 18H, -CH_3), 7.33 (s, 2H, 2'- and 6'-H), 7.37 (m, 2H, 4- and 5-H), 7.44 (d, 1H, *J*12, 1-H), 7.45 (d, 1H, *J*13, 6-H) 7.64 (br s, 1H, -OH) 7.74 (dd, 1H, *J*12 and 3, 2-H), δ_C (DMSO-d_6) 30.07 (-CH_3), 34.61 (-$C(CH_3)_3$), 63.79 (8-C), 115.58, 115.51 (each 9-, 10-C), 124.13 (2'- and 6'-C), 131.02 (1'-C), 132.13 (4-C), 134.31 (1-C), 135.04 (6-C), 139.46 (3'- and 5'-C), 140.70 (2-C), 142.18 (5-C), 155.96 (4'-C), 162.62 (7-C); *m/z* 358 (M^+, base peak).

2.2 Deprotonation of the hydroxyl group

Deprotonation experiments were carried out by adding a small amount of 0.1 *N* sodium hydroxide to solutions of the heptafulvenes **1a-c** sn in DMSO under argon (degassed) while monitoring the absorption spectra, as well as the electrical conductivity of the solution ('conductometric titration').

2.3 MO calculations

Geometry for heptafulvenes **1a-c** and their deprotonated species were optimized by means of the AM1 Hamiltonian in MOPAC94 [10]. The INDO/S program used for spectroscopic calculations is part of the ZINDO program package [11]. Optical absorption bands were then computed on the optimized geometry using the INDO/S Hamiltonian. 145 configurations were considered for the configuration interaction (CI). All calculations were made on a Power Macintosh 8500/120 computer.

2.4 Measurements

Electrical conductivities in solution were measured with a TOA CM-2A conductometer. UV-VIS spectra and IR spectra were recorded on a Shimadzu UV-365 and a Shimadzu IR-440, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer using

TMS as internal standard in either $CDCl_3$ or DMSO (dimethylsulfoxide)-d_6. *J* values are given in Hz. Melting points were determined on a Mettler FP-2 apparatus and are uncorrected.

3. RESULTS

3.1 Conductometric titration and solution spectra

Figure 1 shows the specific conductivity of heptafulvene **1a** solution in DMSO plotted against the molar ratio of sodium hydroxide to heptafulvene **1a**. The conductivity of the solution increases linearly from the start of the titration. This represents the neutralization of the weak acid (heptafulvene **1a**) and the replacement by its salt, which is a strong electrolyte. From point A, the conductivity increases with a higher gradient. This is attributed to the intrinsic conductivity of sodium hydroxide in DMSO. Point A corresponds exactly to the equivalent of heptafulvene **1a**, indicating that the deprotonation proceeded quantitatively. The titration for the heptafulvenes **1b-c** behaves in exactly the same way, as illustrated in Fig. 1.

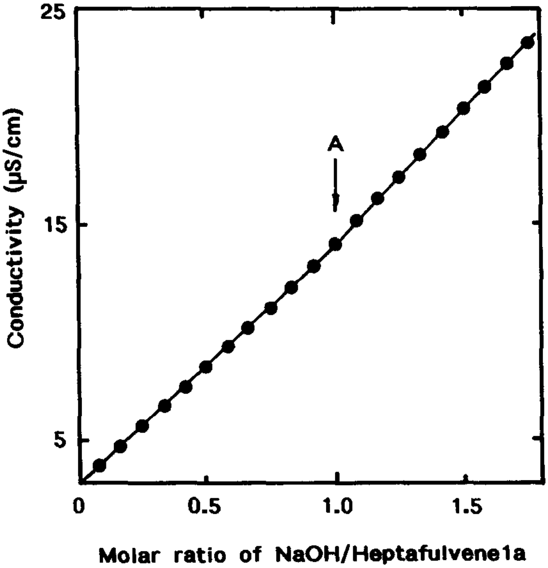


Fig. 1. Conductometric titration of heptafulvene **1a** in DMSO (5.04×10^{-4} M; 100 ml) with sodium hydroxide. Point A denotes the end point.

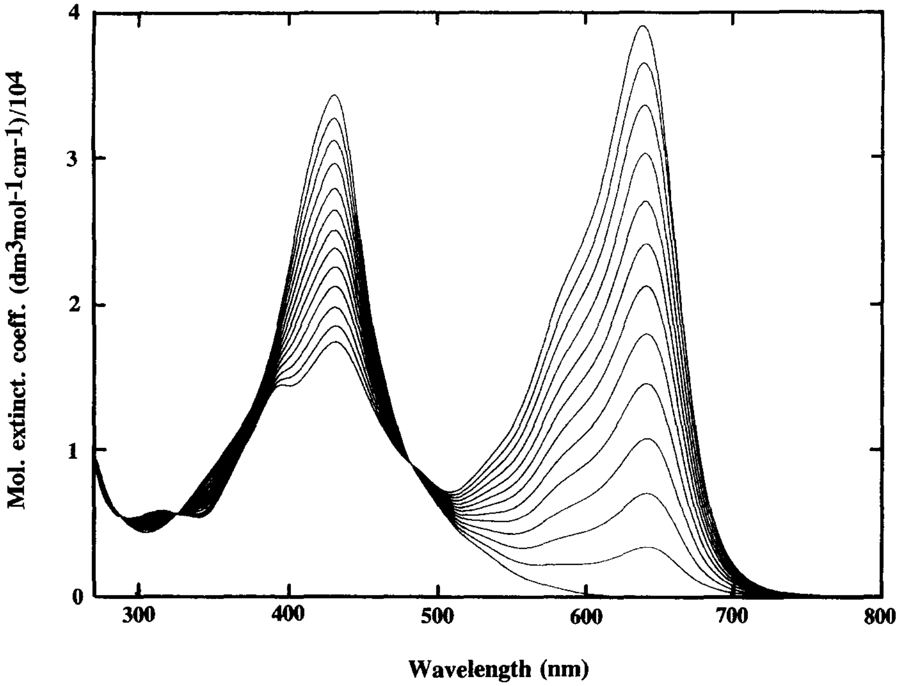


Fig. 2. Solution spectra of heptafulvene **1a** in DMSO as a function of the molar ratio of sodium hydroxide to heptafulvene1a

The absorption spectra of the heptafulvene **1a** from the initial point to point A are shown in Fig. 2. A large spectral shift towards longer wavelengths is observed from 433.7 to 642.7 nm ($\triangle\lambda = 209$ nm; $\triangle(\lambda^{-1}) = 7498$ cm^{-1}). Three isosbestic points are clearly recognized, indicating that the spectral changes are based on a binary equilibrium system, i.e. non-deprotonated and deprotonated states. In fact, the deprotonation reaction is fully reversible as shown by the fact that the addition of hydrochloric acid regenerates the initial state. It should also be noted that the spectral shape of the deprotonated species is very similar to that of the initial spectrum, and that the deprotonation merely displaces the absorption spectrum to longer wavelengths. The spectral change on deprotonation for heptafulvenes **1b-c** proceeded in the same way, as shown in Fig. 2. The spectral displacements are summarized as follows: heptafulvene **1b** (433→661 nm; $\triangle\lambda = 228$ nm, $\triangle(\lambda^{-1}) = 7966$ cm^{-1}) and heptafulvene **1c** (431→662 nm; $\triangle\lambda = 231$ nm, $\triangle(\lambda^{-1}) = 8096$ cm^{-1}).

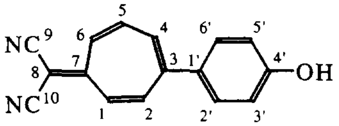
Similar spectra on deprotonation were also obtained in DMF (dimethylformamide) and dioxane, but the optical absorption maxima occurred at shorter wavelengths because of the use of less polar solvents.

3.2 ^{13}C-NMR spectra on deprotonation

Table 1 illustrates the ^{13}C-NMR chemical shifts of the heptafulvene **1a** on deprotonation in DMSO-d_6 at room temperature, together with the calculated formal charges by means of the AM1 Hamiltonian in MOPAC94 [10]. Table 1 also details the proposed peak assignments of the chemical shifts on the basis of the DEPT-spectra (Distortionless Enhancement by Polarization Transfer), as well as of the reported assignments for 8,8-dicyanofulvene [12]. The chemical shifts are represented in ppm relative to tetramethylsilane (TMS). It is significant that the carbon atoms numbered 4, 6, 8, 1′, 3′ (5′) and 4′ are significantly influenced by deprotonation and the carbons atoms numbered 3, 5, 7, 9, 10 and 2′ (6′) are influenced to a lesser extent. On the other hand, the carbons numbered 1 and 2 in the seven-membered ring remain

TABLE 1

^{13}C-NMR Chemical Shifts and Formal Charges of the Carbon Atom on Deprotonation of Heptafulvene **1a**[a]



	Initial State		*Deprotonation*		
No.	*Chemical shift (ppm[b])*	*Formal charge*	*Chemical shift (ppm[b])*	*Formal charge*	*Change in chemical shift (ppm[b])*
1	134.23	-0.0738	134.07	-0.0901	0.16
2	140.61	-0.1320	140.59	-0.1332	0.02
3	150.55	0.0003	152.58	0.1291	-2.03
4	132.20	-0.1129	127.51	-0.2484	**4.69**
5	141.58	-0.1335	140.99	-0.2517	0.59
6	134.49	-0.0752	129.99	-0.0012	**4.50**
7	162.57	0.1015	161.19	0.1624	1.38
8	64.12	-0.0467	57.90	-0.2028	**6.22**
9	115.71	-0.0853	117.32	-0.0407	-1.61
10	115.53	-0.0853	117.23	-0.0354	-1.70
1′	130.33	-0.1033	121.12	0.2747	**9.21**
2′(6′)	129.02	-0.0795	129.99	-0.0208	-0.97
3′(5′)	115.99	-0.1570	120.15	-0.3098	**-4.16**
4′	159.30	0.0922	173.06	0.2904	**-13.76**

[a] The correlation between the ^{13}C-NMR chemical shifts and the formal charges of the carbon atoms gives a coefficient of 0.57, and the correlation is improved to be 0.77 if the values for carbon 8 are excluded.

[b] The chemical shifts are represented in ppm relative to tetramethylsilane (TMS).

almost unchanged. These results clearly indicate that the deprotonation effect ($-O^-$) is not localized only near the oxygen atom, but that the other atoms also receive the effect, leading to the full delocalization of electrons in the chromophore. It should also be noted that the conjugation prevails in the chromophore through the upper half of the seven-membered ring i.e. via carbons 4, 5 and 6.

The correlation between the ^{13}C-NMR chemical shifts and the electron density of the carbon atoms gives a coefficient of 0.57, and the correlation is improved to 0.77 if the values for carbon 3 are omitted.

The heptafulvenes **1b-c** showed the same behavior as described above.

3.3 Molecular conformation

Table 2 illustrates the optimized molecular conformation for the heptafulvenes **1a-c** on deprotonation, together with the calculated optical absorption bands. The seven-membered and phenyl rings are completely planar in all compounds in the initial state, as well as in the deprotonated state, except for the heptafulvene **1c** in which the seven-membered ring is considerably

TABLE 2
Molecular Conformation and Optical Absorption Bands for Heptafulvenes **1a-c**

				Calculated		*Observed*	
Compound	*Heat of formation (Kcal/mol)*	*Dipole moment* (D)	*Torsion angle* (°)	λ *(nm)*	*f* [a]	λ *(nm)*	*logε* [b]
Heptafulvene **1a** (initial)	104.98	6.63	45.00	336[c]	0.716	434	4.54
				394[c]	0.338		
Heptafulvene **1a** (deprotonated)	62.77	3.74	25.27	541	1.246	643	4.60
Heptafulvene **1b** (initial)	92.14	7.07	45.37	372	1.068	433	4.43
Heptafulvene **1b** (deprotonated)	49.01	2.14	26.04	556	1.246	661	4.72
Heptafulvene **1c** (initial)	75.60[d]	6.53	52.16	368[c]	0.526	431	4.56
				361[c]	0.415		
Heptafulvene **1c** (deprotonated)	31.84	4.21	28.12	555	1.208	662	4.86

[a] Oscillator strength.

[b] Molar extinction coefficient.

[c] Major CI components: **1a** (initial) 336nm: (45→46)/(45→47) 394nm: (45→46)/(45→47) **1c** (initial) 368nm: (69→71)/(69→70) 361nm: (69→70)/(69→71) where the number refers to the molecular orbital, and the arrow denotes the transition from one orbital to another.

[d] The seven-membered ring is considerably deformed.

deformed only in the initial state. The torsion angle between the seven-membered ring and the phenyl ring amounts to about 45–52° in the initial state. Deprotonation, however, reduces the twisted angle by about 20°, which results in a larger overlapping of π orbitals between the two rings.

The initial state in the heptafulvenes **1a-c** is also characterized by a large dipole moment of about 7 *D*, whereas these values become notably smaller on deprotonation, accompanied by a reduction in the heat of formation. This indicates that the electrons are delocalized and that the two-ring system is thus stabilized.

3.4 Optical absorption bands

The computed optical absorption spectra are also given in Table 2, together with the oscillator strengths for the heptafulvenes **1a-c**. The optical absorption bands appear in the wavelength region around 360–400 nm in the initial state. No appreciable difference in absorption maximum is apparent for the three different substituents (R = H, CH_3 and *tert*-Bu) whose electron-donating ability increases in this order. The major component of the optical absorption band is assigned to the π-π^* transition from the HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) in all compounds, except for the initial state of the heptafulvenes **1a** and **1c**. There are two electronic transitions in the initial state of the heptafulvene **1a**, each of which includes the two major CI-components: the transitions 45→46 (HOMO→LUMO) and 45→47, where the number refers to the molecular orbital. Similarly, the two transitions in the heptafulvene **1c** are composed of the two CI components with an almost equal weight, viz. the transitions 69→79 (HOMO→LUMO) and 69→71. Deprotonation displaces significantly the absorption bands towards longer wavelengths in all compounds, accompanying an increase in oscillator strength.

4 DISCUSSION

4.1 Change in molecular conformation

The seven-membered ring and the phenyl ring are twisted by about 45–52° in the initial state, as shown in Table 2. The present situation is very similar to that of biphenyl, in which the torsion angle is about 40.10° according to our geometry optimization by the AM1 Hamiltonian. The two phenyl rings are twisted, mainly because the two opposing hydrogen atoms at the ortho position (2,2′, 6,6′) repel each other. This is, however, balanced by a force to stabilize the system through possible electron conjugation between the two phenyl rings. In the case of 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvene, the steric repulsion between the hydrogen atoms is more pronounced, because one of the rings is seven-membered. This explains qualitatively that the torsion angle is larger in the heptafulvenes **1a-c** (45-53°) than in biphenyl (40.10°).

Deprotonation gives the oxygen atom a negative charge ($-O^-$) which is in turn fully delocalized in the chromophore, as shown by the change in the ^{13}C-NMR chemical shifts shown in Table 1. The increased delocalization implies that the electron conjugation is enhanced between the seven-membered ring and the phenyl ring. This is also consistent with the reduction in torsion angle on deprotonation, as shown in Table 2.

4.2 Optical absorption bands and bathochromic shifts

It is apparent from Fig. 2 and Table 2 that there is a good qualitative agreement between the observed and calculated optical absorption bands, although the computed wavelengths are underestimated. In the initial state, the absorption maxima of heptafulvenes **1a-c** in Fig. 2 appear at 434, 433 and 431 nm, respectively. On deprotonation, the corresponding absorption bands are displaced to 643, 661 and 662 nm. The present tendency is well reproduced in the computed absorption spectra.

The large bathochromic shift on deprotonation can also be interpreted in the following way. The major contribution is due to the increased electron density in the chromophore. In the initial state, a pair of electrons are shared by oxygen and hydrogen atoms to form a covalent bond. Deprotonation displaces one bonded electron onto the oxygen atom ($-O^-$) which leads to the increase in electron density on the oxygen atom. This electron is then delocalized in the chromophore, as is evident from the change in chemical shifts in the ^{13}C-NMR spectra (Table 1). The thus increased electron density in the chromophore explains why the optical absorption band is considerably displaced towards longer wavelengths. The increase in electron density also induces the reduction in the torsion angle between the seven-membered ring and the phenyl ring, leading to the bathochromic displacement.

4.3 Substitutent effects on the optical absorption

Both the observed and calculated absorption bands (Table 2) for three different derivatives **1a-c** ($R = H$, CH_3 and *tert*-Bu) gave no substantial difference in absorption maxima in solution. In the solid state, however, there is a distinct difference in color between the heptafulvenes **1a-b** and **1c**. The former two are colored orange, whereas the latter exhibits a dark wine color. This is assumed to arise from intermolecular interactions in the solid state. Further investigation is now in progress, on the basis of crystal structure analysis.

5 CONCLUSIONS

Some new 8,8-dicyano-3-(4′-hydroxy)phenylheptafulvenes have been synthesized and their electronic spectra have been characterized in solution, with major focus on the spectral and conformational change on deprotonation. MO calculations revealed that the seven-membered ring and the phenyl ring are twisted by about 45–52° in the initial state. Deprotonation, however, greatly reduces the torsion angle by about 20°, enhancing the electron conjugation of the system. Deprotonation gives the oxygen atom a negative charge ($-O^-$), which is in turn delocalized in the chromophore. The bathochromic displacement on deprotonation can be interpreted as being due to the increased electron density in the chromophore, accompanied by the conjugation enhancement between the seven-membered ring and the phenyl ring.

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