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Synthesis, structure and second-order nonlinear optical properties of highly functionalized 6-aminopentafulvenes

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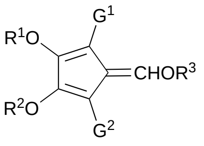
Novel donor–acceptor functionalized pentafulvenes have been synthesized and characterized. Structural data have been obtained by single crystal X-ray diffraction. Their molecular and macroscopic second-order nonlinear optical properties have been investigated, *via* electric field induced second harmonic generation (EFISH) in solution and by second harmonic generation with evanescent wave (SHEW) in the solid state.

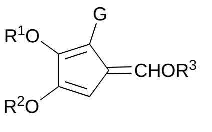
In the last few years, much attention has been paid to the synthesis and characterization of highly conjugated non-centrosymmetric molecular systems, for second-order nonlinear optical applications.[1] In fact, it is well documented that highly polarizable push–pull systems present large second-order molecular polarizabilities. In many systems investigated the high conjugation is provided by benzene rings. Pentafulvene (referred to hereafter as fulvene) is an isomer of benzene, but with a very different electronic structure. In particular, its ground state presents a strong polyolefinic character as compared to the aromaticity associated with the benzene ring. Moreover, whereas functionalized benzenes keep their aromatic character, the π-conjugation degree in fulvenes is markedly dependent on the nature of the substituents. As an example, the π-electronic delocalization is strongly enhanced when moving from the 6-alkyl or 6-aryl to the 6-amino substituted fulvenes.

Many different substituted fulvenes have been described.[2] The synthesis and the structure of highly functionalized 2,3,6-trioxyfulvenes, **1** and **2**, have been reported by the Barcelona group.[3] These new systems include donor and acceptor substituents directly attached to the ring, that give rise to well-defined push–pull patterns.



1

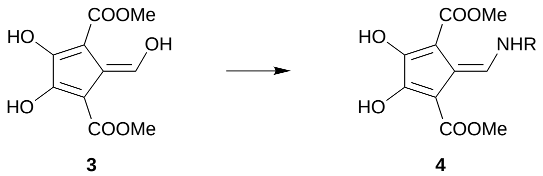
G^1 = COOMe, CN
G^2 = COOMe, CN, NO_2, Ts
R = Me, H



2

G = COOMe
R^1, R^2 = Ac, Me
R^3 = Me, H

More recently, 6-aminofulvenes **4** have been obtained from 2,3,6-trihydroxyfulvene **3** by nucleophilic substitution[4] (Scheme 1).

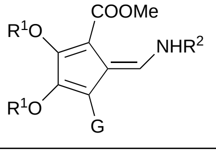


R = Me, Bu, cyclohexyl, cyclooctyl, Ph
p-$MeOC_6H_4$, p-$Bu^sC_6H_4$

Scheme 1

A few theoretical and experimental studies on the second-order nonlinear optical properties of some fulvenes have been published.[5]

We present here the synthesis of three new series of highly functionalized 6-aminofulvenes **5–7**, analogues of compounds **4**, using the cited procedure.[4] The second-order polarizabilities β of 6-aminofulvenes **4–7** as well as of three 6-azafulvenes **8**[6] (similar to 6-aminofulvenes **7**) have been measured. For some of these molecules, structure determinations by single crystal X-ray diffraction have been carried out in order to obtain information about their electronic delocalization and so provide additional information on the molecular behaviour.



$R^1 = H$		$R^1 = Me$	
G = COOMe	G = CN	G = COOMe	G = CN
4a $R^2 = Ph$	**5a** $R^2 = Ph$	**6a** $R^2 = Ph$	**7a** $R^2 = Ph$
4b $R^2 = p$-$MeOC_6H_4$	**5b** $R^2 = p$-$MeOC_6H_4$	**6b** $R^2 = p$-$MeOC_6H_4$	**7b** $R^2 = p$-$MeOC_6H_4$
4c $R^2 = Me$	**5c** $R^2 = Me$	**6c** $R^2 = Me$	**7c** $R^2 = Bu$
4d $R^2 = HOCH_2MeCH$		**6d** $R^2 = HOCH_2MeCH$	**7d** $R^2 = HOCH_2MeCH$
		6e $R^2 = p$-$Me_2NC_6H_4$	

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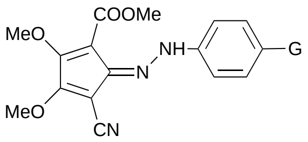
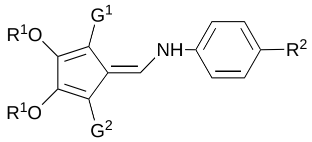
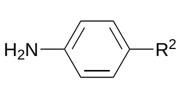


8a G = NO_2
b G = CN
c G = H

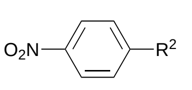
One aim of our work has been to correlate the measured β values with the molecular structure and the nature of the substituents. From this analysis some guidelines have been obtained for optimizing the nonlinear behaviour of these functionalized fulvenes. Following these guidelines and using the chiral amines **10g–h** we have synthesized the 6-aminofulvenes **4g–h**, **5g–h**, **6g–h** and **9g–h**. Some of them exhibit significant second-order NLO properties in the solid state.



R^1=H		R^1=Me	
G^1, G^2=COOMe	G^1=COOMe, G^2=CN	G^1, G^2=COOMe	G^1=COOMe, G^2=CN
4g **4h**	**5g** **5h**	**6g** **6h**	**9g** **9h**

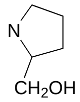


10g, h

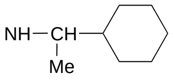


11g, h

4–11g R^2 =



4–11h R^2 =



Experimental

The compounds were characterized by elemental analysis, mass spectrometry, IR and UV–VIS spectroscopy and nuclear magnetic resonance (NMR). UV–VIS measurements were carried out on a Hewlett-Packard 8450A spectrophotometer. IR spectra were recorded on a Perkin Elmer 683 or on a Bomem Michelson 100 (FTIR) instrument. Mass spectra were determined on Hewlett-Packard 5995A and 5998A spectrometers. NMR spectra were obtained with a Perkin Elmer R-24 (^1H NMR, 60 MHz), a Bruker AC-80 (^1H NMR, 80 MHz; ^{13}C NMR, 20.1 MHz), a Varian XL-200/F-19 and a Bruker AC-200 (^1H NMR, 200 MHz; ^{13}C NMR, 50.3 MHz) and a Varian Gemini-300 (^1H NMR, 300 MHz; ^{13}C NMR, 75.5 MHz). *J* values are in Hz, and tetramethylsilane was used as reference. The EFISH technique reported elsewhere[7] was used to determine the second-order polarizabilities β. The light source was a Q-switched Nd^{3+}:YAG laser operating at 1.34 μm, with 60 ns pulse duration. The incident beam was focused onto a liquid cell and synchronized with a DC field applied to the solution containing the nonlinear molecules. The experiments were performed in chloroform solutions at different concentrations. By looking at the concentration dependence of the second-harmonic intensity, the sign of β was determined,[8] that of the solvent being known. The value measured by this technique is the product of the β_{zzz} component of the β tensor by the ground state dipole moment, μ, directed along the *z* axis. This was independently determined from capacitance measurements, by a classical method based on the Guggenheim theory.[9] The third-order electronic contribution γ_e has been neglected in comparison with the orientational term $(\mu\ \beta_{zzz})/(5\ kT)$ in the expression $\gamma^{EFISH}=\gamma_e+(\mu\ \beta_{zzz})/(5\ kT)$.

The SHEW technique reported elsewhere[10] was used to evaluate the nonlinear optical properties in the solid state. The compound was crushed to a fine powder and placed in contact with a surface of a total reflection prism made of rutile. The fundamental wave of a Q-switched Nd $^{3+}$:YAG laser (λ= 1.064 μm) was guided into the prism and was totally reflected at the boundary. The reflected second-harmonics were detected and their power was compared with that of *m*-nitroaniline measured under the same conditions. In this way, effective values of the optical second-order coefficient, d_{eff}, relative to that for *m*-nitroaniline were obtained. The d_{eff} value is close to the largest component of the *d* tensor.

Synthesis of chiral *p*-phenylenediamines 10

(*S*)-*N*-(*p*-Aminophenyl)prolinol 10g. To a mixture of 300 mg (1.35 mmol) of (*S*)-*N*-(*p*-nitrophenyl)prolinol[11] in 16 ml of methanol and 5.4 ml of saturated cupric acetate solution was added slowly 540 mg (14.3 mmol) of sodium borohydride. Then 32 ml of diethyl ether was added. The reaction mixture was washed with sodium hydrogen carbonate solution and extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Mp 85 °C (yield 68%). $[\alpha]_D^{25}-89.3$ ($CHCl_3$) (Found: C 68.62, H 8.61, N 14.59. Calc. for $C_{11}H_{16}ON_2$: C 68.72, H 8.39, N 14.57%). δ_H (300 MHz, $CDCl_3$): 6.67–6.60 (4H, m, 4 CH ar), 3.77–3.68 (1H, m, CH), 3.67 (1H, d × d, ^3J 5, ^2J 10, CH_aH_bOH), 3.58 (1H, d × d, ^3J 4, ^2J 10, CH_aH_bOH), 3.54–3.45 (1H, m, CH_aH_bN), 3.25 (deuterium exchangeable, br, NH_2, NH, OH), 3.11–3.00 (1H, m, CH_aH_bN), 2.10–1.88 (4H, m, CCH_2CH_2C). δ_C (75.5 MHz, $CDCl_3$): 142.1 (C4 ar), 136.9 (C1 ar), 117.0 (C2 ar), 113.9 (C3 ar), 64.2 (CH_2OH), 60.7 (N-CH), 50.6 (N-CH_2), 28.9 (NCHCH_2), 24.0 (NCH_2CH_2). $\bar{\nu}_{max}/cm^{-1}$ (KBr): 3400–3180 ($\nu_{O\text{-}H}$, $\nu_{N\text{-}H}$). MS, *m*/*z* 192, (14%) (M), 162 (12), 161 (M − 31) (100), 119 (14), 65 (13). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 253 (4.0), 330 (3.3).

(*R*)-*N*-(1-Cyclohexylethyl)-*p*-nitroaniline 11h. A solution of 1.04 g (7 mmol) of 1-fluoro-4-nitrobenzene in 0.8 ml of dimethyl sulfoxide was added slowly to a mixture of 1 g (8 mmol) of (*R*)-1-cyclohexylethylamine, 1 ml of dimethyl sulfoxide and 2.21 g (16 mmol) of potassium carbonate. The mixture was stirred at 50 °C for 24 h. The reaction mixture was poured into water and extracted with methylene chloride. The organic layer was dried ($MgSO_4$) and the solvent was removed on reduced pressure. The residue was chromatographed on silica gel (eluent, AcOEt–hexane, 1 : 2) to give the product **11h**. Mp 65 °C (yield 67%). $[\alpha]_D^{25}$ 15.9 ($CHCl_3$) (Found: C 67.65, H 8.23, N 11.05. Calc. for $C_{14}H_{20}O_2N_2$: C 67.70, H 8.12, N 11.29%). δ_H (300 MHz, $CDCl_3$): 8.06, 6.49 (4H, m, 4 CH ar), 4.50 (1H, deuterium exchangeable, br, NH), 3.46–3.41 (1H, m, *C*HMe), 1.86–0.92 (11H, m, cyclohexyl-H), 1.17 (3H, d, ^3J 7, CH_3). δ_C (75.5 MHz, $CDCl_3$): 153.0 (C4 ar), 137.3 (C1 ar), 126.6 (C2 ar), 111.0 (C3 ar), 53.1 (*C*H-Me), 43.1, 29.5, 28.6, 26.4, 26.2, 26.1 (cyclohexyl-C), 17.4 (CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3360 ($\nu_{N\text{-}H}$), 1530 and 1305 ($\nu_{N\text{-}O}$). MS, *m*/*z*: 248 (7%) (M), 165 (100), 119 (25), 41 (12). UV, λ_{max}/nm (log ε) CH_2Cl_2): 382 (4.3).

(*R*)-*N*-(1-Cyclohexylethyl)-*p*-phenylenediamine 10h. To a mixture of 376 mg (1.52 mmol) of the nitroaniline **11h** in 18 ml of methanol and 6 ml of saturated cupric acetate solution cooled to 0 °C was added slowly 600 mg (15.9 mmol) of sodium borohydride. Then 36 ml of diethyl ether was added. The reaction mixture was washed with sodium hydrogen carbonate solution and extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was chromatographed on alumina (eluent, AcOEt–hexane, 1 : 5) to give the product **10h** as an oil (yield 45%) (Found: C 77.22, H 10.38, N 12.55. Calc. for $C_{14}H_{22}N_2$: C 77.01, H 10.16, N 12.83%). δ_H (300 MHz, $CDCl_3$): 6.59–6.47 (4H, m, 4 CH ar), 3.11 (3H, deuterium exchangeable, br, NH), 3.19 (1H, m, C*H*Me), 1.86–0.92 (11H, m, cyclohexyl-H), 1.07 (3H, d, ^3J 7, CH_3). δ_C (75.5 MHz, $CDCl_3$): 141.1 (C4 ar), 137.1 (C1 ar), 117.0 (C2 ar), 115.0 (C3 ar), 42.8, 29.8, 28.1, 26.7, 26.5, 26.3 (cyclohexyl-C_6), 17.3 (CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3450–3150 ($\nu_{N\text{-}H}$). MS, *m/z* 218 (16%) (M), 135 (100), 107 (11), 46 (10). UV, λ_{max}/nm (log ε)(CH_2Cl_2): 250 (4.2), 329 (3.4).

Synthesis of dimethyl 6-amino-2,3-dihydroxyfulvene-1,4-dicarboxylates 4

The compounds **4a–c** have been described elsewhere.[4]

General procedure

To a suspension of dimethyl 2,3,6-trihydroxyfulvene-1,4-dicarboxylate (100 mg, 0.41 mmol) in 3 ml of methylene chloride, an equimolar amount of the appropriate amine was added. The mixture was stirred at room temp. until no fulvene could be detected by TLC (between 2 and 5 h, depending on the amine). The solvent was removed under reduced pressure to yield the corresponding amino compound, which was purified by recrystallization or by chromatography.

Dimethyl 2,3-dihydroxy-6-(2-hydroxy-1-methylethylamino)-fulvene-1,4-dicarboxylate 4d. Recrystallized from acetone. Mp 159–160 °C (yield 56%) (Found: C 52.02, H 5.80, N 4.79. Calc. for $C_{13}H_{17}O_7N$: C 52.17, H 5.73, N 4.68%). δ_H (60 MHz, CD_3COCD_3): 9.90 (1H, deuterium exchangeable, br, NH), 8.20 (1H, d, *J* 14, C6-H), 3.90 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 3.60 (3H, m, $CHCH_2$), 1.35 (3H, d, *J* 6, CH_3). MS, *m/z* 299 (55%) (M), 267 (97), 236 (57), 235 (54), 207 (100), 204 (42), 176 (46), 148 (22), 139 (15), 66 (12), 59 (12), 55 (18), 39 (14). UV, λ_{max}/nm (log ε) (CH_3CN): 239 (4.0), 346 (3.2), 436 (4.2).

Dimethyl (*S*)-2,3-dihydroxy-6-[4-(2-hydroxymethylpyrrolidin-1-yl)anilino]fulvene-1,4-dicarboxylate 4g. Recrystallized from acetone. Mp 240 °C (yield 97%) (Found: C 60.10, H 5.97, N 6.38. Calc. for $C_{21}H_{24}O_7N_2$: C 60.57, H 5.81, N 6.73%). δ_H (300 MHz, $CDCl_3$): 11.67 (1H, deuterium exchangeable, br, NH), 9.05 (1H, deuterium exchangeable, br, O-H), 8.56 (1H, d, *J* 13, C6-H), 7.07–6.69 (4H, m, C_6H_4), 4.01 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 3.90–3.82 (1H, m, N-CH), 3.68–3.66 (2H, m, CH_2OH), 3.56–3.50 (1H, m, N-CH_aH_b), 3.20–3.10 (1H, m, N-CH_aH_b), 2.10–1.95 (4H, m, $NCH_2CH_2CH_2$). δ_C (75.5 MHz, $CDCl_3$): 167.6 ($COOCH_3$), 167.0 ($COOCH_3$), 151.0 and 149.7 (C2 and C3), 145.1 (C4 ar), 137.4 (C6), 130.4 (C1 ar), 117.8 (C2 ar), 113.3 (C3 ar), 105.1 and 103.7 (C4 and C5), 100.2 (C1), 63.9 (CH_2OH), 60.4 (N-CH), 52.1 ($COOCH_3$), 51.5 ($COOCH_3$), 49.8 (N-CH_2), 28.8 (N-CH_2-CH_2-CH_2), 23.8 (N-CH_2-CH_2-CH_2). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3500–2500 ($\nu_{O\text{-}H}$), 1640 ($\nu_{C=O}$ $COOCH_3$). MS, *m/z* 416 (4%) (M), 384 (10), 353 (15), 301 (10), 283 (29), 171 (88), 84 (22), 83 (29), 71 (34), 70 (34), 69 (48), 67 (12), 57 (78), 56 (32), 55 (80), 44 (100), 43 (82), 42 (25), 41 (91), 39 (42). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 258 (4.1), 306 (4.1), 494 (4.2).

Dimethyl (*R*)-6-[4-(1-cyclohexylethylamino)anilino]-2,3-dihydroxyfulvene-1,4-dicarboxylate 4h. Chromatographed on silica gel (eluent, AcOEt-hexane, 1 : 2). Oil (yield 95%) (Found: C 65.50, H 6.91, N 6.37. Calc. for $C_{24}H_{30}O_6N_2$: C 65.14, H 6.83, N 6.33%). δ_H (300 MHz, CD_3COCD_3): 11.76 (1H, deuterium exchangeable, d, *J* 13, NH), 9.07 (1H, deuterium exchangeable, br, OH), 8.64 (1H, d, *J* 13, C6-H), 7.01–6.68 (4H, m, C_6H_4), 4.00 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 3.40–3.30 (1H, m, NCH), 1.86–0.92 (11H, m, cyclohexyl-H), 1.12 (3H, d, *J* 6, CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3500–2500 ($\nu_{O\text{-}H}$, $\nu_{N\text{-}H}$), 1650 ($\nu_{C=O}$ $COOCH_3$). MS, *m/z*, 442 (16%) (M), 410 (19), 378 (21), 327 (20), 295 (47), 171 (88), 84 (22), 83 (29), 71 (34), 70 (34), 69 (48), 67 (12), 57 (78), 56 (32), 55 (80), 44 (100), 43 (82), 42 (25), 41 (91), 39 (42). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 250 (3.7), 296 (3.7), 350 (3.5), 489 (3.8).

Synthesis of methyl 6-amino-4-cyano-2,3-dihydroxyfulvene-1-carboxylates 5

General procedure

To a suspension of methyl (*Z*)-4-cyano-2,3,6-trihydroxyfulvene-1-carboxylate (100 mg, 0.48 mmol) in 3 ml of dry diethyl ether, an equimolar amount of the appropriate amine was added. The mixture was stirred at room temperature until no fulvene was detected by TLC (between 15 min and 48 h, depending on the amine). The solvent was removed under reduced pressure to yield the corresponding amino compound. Solids were recrystallized from acetone.

Methyl (*Z*)-6-anilino-4-cyano-2,3-dihydroxyfulvene-1-carboxylate 5a. Mp 205 °C (decomp) (yield 72%) (Found: C 63.65, H 4.22, N 9.80. Calc. for $C_{15}H_{12}O_4N_2$: C 63.38, H 4.25, N 9.85%). δ_H (200 MHz, CD_3COCD_3): 11.70 (1H, deuterium exchangeable, d, *J* 13, NH), 7.62 (1H, d, *J* 13, C6-H), 7.43–7.10 (5H, m, 5 CH ar), 3.99 (3H, s, OCH_3). δ_C (50.3 MHz, CD_3COCD_3): 167.2 ($COOCH_3$), 154.7 and 150.6 (C2 and C3), 136.5 (C1 ar), 134.5 (C6), 130.8 (C3 ar), 124.4 (C4 ar), 116.7 (C2 ar), 115.1 (CN), 107.9 (C5), 99.6 (C1), 90.0 (C4), 52.5 ($COOCH_3$). $\bar{\nu}_{max}/cm^{-1}$ (KBr): 3500–2500 ($\nu_{O\text{-}H}$), 2220 (ν_{CN}), 1665 ($\nu_{C=O}$ $COOCH_3$). MS, *m/z* 284 (27%) (M), 252 (100), 224 (48), 223 (12), 195 (11), 168 (40), 167 (29), 140 (24), 129 (13), 104 (25), 91 (13), 77 (78), 65 (11), 51 (27). UV, λ_{max}/nm (log ε) (CH_3CN): 249 (4.1), 430 (4.4).

Methyl (*Z*)-6-anisidino-4-cyano-2,3-dihydroxyfulvene-1-carboxylate 5b. Mp 204 °C (decomp.) (yield 78%) (Found: C 61.24, H 4.60, N 8.78. Calc. for $C_{16}H_{14}O_5N_2$: C 61.14, H 4.49, N 8.91%). δ_H (80 MHz, CD_3COCD_3): 11.60 (1H, deuterium exchangeable, d, *J* 13, NH), 7.55 (1H, d, *J* 13, C6-H), 7.29–6.93 (4H, m, 4 CH ar), 3.99 (3H, s, OCH_3), 3.81 (3H, s, OCH_3). δ_C (50.3 MHz, $CDCl_3$): 167.3 ($COOCH_3$), 157.5 (C4 ar), 154.0 and 149.8 (C2 and C3), 135.9 (C6), 134.2 (C1 ar), 118.4 (C2 ar), 116.0 (C3 ar), 115.1 (CN), 107.3 (C5), 99.6 (C1), 90.1 (C4), 55.8 (OCH_3), 52.4 ($COOCH_3$). $\bar{\nu}_{max}/cm^{-1}$ (KBr): 3500–2500 ($\nu_{O\text{-}H}$), 2210 (ν_{CN}), 1660 ($\nu_{C=O}$ $COOCH_3$). MS, *m/z* 314, (30%) (M), 282 (100), 254 (19), 198 (9), 108 (9). UV, λ_{max}/nm (log ε) (CH_3CN): 249 (4.1), 277 (3.9), 440, (4.4).

Methyl (*Z*)-4-cyano-2,3-dihydroxy-6-methylaminofulvene-1-carboxylate 5c. Mp 186–187 °C (Yield 35%) (Found: C 54.21, H 4.61, N 12.52. Calc. for $C_{10}H_{10}O_4N_2$: C 54.06, H 4.54, N 12.61%). δ_H (60 MHz, CD_3COCD_3): 9.50 (1H, deuterium exchangeable, br, NH), 7.16 (1H, d, *J* 13, C6-H), 3.90 (3H, s, OCH_3), 3.26 (3H, d, *J* 5, N-CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from acetone): 3500–2500 ($\nu_{O\text{-}H}$), 2210 (ν_{CN}), 1660 ($\nu_{C=O}$ $COOCH_3$). UV, λ_{max}/nm (log ε)(CH_3CN): 242 (4.1), 352 (3.8), 410 (4.2).

Methyl (*S*)-(*Z*)-4-cyano-2,3-dihydroxy-6-[4-(2-hydroxymethylpyrrolidin-1-yl)anilino]fulvene-1-carboxylate 5g. Mp 208 °C (Yield 83%) (Found: C 62.61, H 5.52, N 11.07. Calc. for $C_{20}H_{21}O_5N_3$: C 62.65, H 5.52, N 10.96%). δ_H (300 MHz, CD_3COCD_3): 11.73 (1H, deuterium exchangeable, d, *J* 13, NH), 7.56 (1H, d, *J* 13, C6-H), 7.17–6.72 (4H, m, C_6H_4), 3.98 (3H, s, OCH_3), 3.84–3.75 (1H, m, NCH), 3.67 (1H, d × d, ^2J 11, ^3J 3, CH_aH_bOH), 3.50–3.45 (1H, m, N-CH_aH_b), 3.41 (1H, d × d, ^2J 11, ^3J 8, CH_aH_b OH), 3.18–3.07 (1H, m, NCH_aH_b), 2.17–1.94 (4H, m, $NCH_2CH_2CH_2$). δ_C (75.5 MHz, CD_3COCD_3): 167.4 ($COOCH_3$), 152.8 and 148.5 (C2 and C3), 146.3 (C4 ar), 136.3 (C6), 129.9 (C1 ar), 118.6 (C2 ar), 115.4 (CN), 113.8 (C3 ar), 106.9 (C5), 99.4 (C1), 90.1 (C4), 62.9 (CH_2OH), 61.6 (NCH), 52.4 (COO*C*H$_3$), 49.6 (NCH_2), 29.8 (NCH$_2$CH$_2$*C*H$_2$), 23.9 (NCH$_2$*C*H$_2$CH$_2$). $\bar{\nu}_{max}$/cm^{-1} (KBr): 3500–2500 ($\nu_{O\text{-}H}$), 2190 (ν_{CN}), 1655 ($\nu_{C=O}$ COOCH$_3$). MS, *m/z*, 383 (1%) (M), 320 (16), 71 (14), 69 (17), 57 (28), 55 (30), 44 (100), 41 (34). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 253 (4.2), 295 (4.0), 340 (3.9), 480 (4.4).

Methyl (*R*)-(*Z*)-4-cyano-6-[4-(1-cyclohexylethylamino]anilino]-2,3-dihydroxyfulvene-1-carboxylate 5h. Chromatographed on silica gel (eluent, AcOEt–hexane, 1:2). Oil (yield 54%), (Found: C 67.92, H 6.72, N 10.15. Calc. for $C_{23}H_{27}O_4N_3$: C 67.46, H 6.65, N 10.26%). δ_H (300 MHz, CD_3COCD_3): 11.71 (1H, deuterium exchangeable, d, *J* 13, NH), 7.54 (1H, d, *J* 13, C6-H), 7.12–6.83 (4H, m, C_6H_4), 3.98 (3H, s, OCH_3), 3.45–3.30 (1H, m, NCH), 1.86–0.92 (11H, m, cyclohexyl-H), 1.15 (3H, d, *J* 6, CH_3). δ_C (75.5 MHz, CD_3COCD_3): 167.4 (*C*OOCH$_3$), 153.0 and 148.8 (C2 and C3), 145.0 (C4 ar), 135.9 (C6), 131.2 (C1 ar), 118.6 (C2 ar), 116.0 (C3 ar), 115.3 (CN), 107.0 (C5), 99.4 (C1), 90.1 (C4), 55.1 (N-CH), 52.4 (COO*C*H$_3$), 43.4, 30.5, 28.9, 27.2, 27.1, 27.0 (cyclohexyl-C_6), 16.9 (CH_3). $\bar{\nu}_{max}$/cm^{-1} (film evaporated from acetone): 3500–2500 ($\nu_{O\text{-}H}$, $\nu_{N\text{-}H}$), 2200 (ν_{CN}), 1665 ($\nu_{C=O}$COOCH$_3$). MS, *m/z* 409 (1%) (M), 377 (20), 110 (31), 95 (20), 82 (24), 81 (100), 69 (19), 68 (20), 67 (78), 65 (19), 55 (36), 53 (35), 44 (46), 41 (60). UV λ_{max}/nm (log ε) (CH_2Cl_2): 240 (3.8), 286 (3.7), 340 (3.5), 474 (3.9).

Synthesis of dimethyl 6-amino-2,3-dimethoxyfulvene-1,4-dicarboxylates 6

General procedure

To a solution of 100 mg (0.37 mmol) of dimethyl 6-hydroxy-2,3-dimethoxyfulvene-1,4-dicarboxylate in 3 ml dry diethyl ether, an equimolar amount of the appropriate amine was added. The mixture was stirred at room temperature for 15–120 min (depending on the amine, reaction monitored by TLC). The solvent was removed under reduced pressure and finally the residue was chromatographed on silica gel (eluent, AcOEt–hexane, 1:4) to give the corresponding amino compound.

Dimethyl 6-anilino-2,3-dimethoxyfulvene-1,4-dicarboxylate 6a. Mp 94–96 °C (yield 85%) (Found: C 62.50, H 5.70, N 3.96. Calc. for $C_{18}H_{19}O_6N$: C 62.60, H 5.55, N 4.06%). δ_H (80 MHz, $CDCl_3$): 12.92 (1H, deuterium exchangeable, d *J* 13, NH), 9.26 (1H, d, *J* 13, C6-H), 7.49–7.02 (5H, m, 5 CH ar), 3.96 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3,89 (3H, s, OCH_3). δ_C (50.3 MHz, $CDCl_3$): 168.1 (*C*OOCH$_3$), 165.2 (*C*OOCH$_3$), 155.4 and 150.6 (C2 and C3), 143.4 (C6), 139.7 (C1 ar), 129.8 (C3 ar), 124.7 (C4 ar), 117.1 (C2 ar), 113.3 (C4), 107.2 (C5), 106.2 (C1), 61.7 (OCH_3), 61.4 (OCH_3), 52.2 (COO*C*H$_3$), 51.5 (COO*C*H$_3$). $\bar{\nu}_{max}$/cm^{-1} (film evaporated from $CHCl_3$): 1700 ($\nu_{C=O}$ C4-COOCH$_3$), 1640 ($\nu_{C=O}$ C1-COOCH$_3$). MS, *m/z* 346 (21%) (M + 1), 345 (100) (M), 314 (19), 313 (60), 298 (95), 283 (16), 266 (21), 223 (11), 77 (14). UV, λ_{max}/nm (log ε) (CH_3CN): 239 (4.3), 436 (4.5).

Dimethyl 6-anisidino-2,3-dimethoxyfulvene-1,4-dicarboxylate 6b. Mp 123–124 °C (yield 88%) (Found: C 60.77, H 5.94, N 3.61. Calc. for $C_{19}H_{21}O_7N$: C 60.79, H 5.64, N 3.73%. δ_H (80 MHz, $CDCl_3$): 12.98 (1H, deuterium exchangeable, d, *J* 14, NH), 9.20 (1H, d, *J* 14, C6-H), 7.25–6.82 (4H, m, 4 CH ar.), 3.95 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 3.89 (6H, s, 2 OCH_3), 3.78 (3H, s, OCH_3 ar). δ_C (50.3 MHz, $CDCl_3$): 168.1 (*C*OOCH$_3$), 165.1 (*C*OOCH$_3$), 157.1 (C4 ar), 154.7 and 150.0 (C2 and C3), 143.8 (C6), 133.1 (C1 ar), 118.4 (C2 ar), 115.0 (C3 ar), 113.0 (C4), 106.9 (C5), 105.7 (C1), 61.4 (OCH_3), 61.2 (OCH_3), 55.4 (C4ar-O*C*H$_3$), 51.8 (COO*C*H$_3$), 51.1 (COO*C*H$_3$), $\bar{\nu}_{max}$/cm^{-1} (film evaporated from $CHCl_3$): 1690 ($\nu_{C=O}$ C4-COOCH$_3$), 1635 ($\nu_{C=O}$ C1-COOCH$_3$). MS, *m/z* 376 (22%) (M + 1), 375 (100) (M), 344 (16), 343 (58), 329 (17), 328 (89), 296 (16), 253 (12). UV, λ_{max}/nm (log ε) (CH_3CN): 238 (4.4), 444 (4.5).

Dimethyl 2,3-dimethoxy-6-methylaminofulvene-1,4-dicarboxylate 6c. Mp 119–120 °C (yield 96%) (Found: C 55.11, H 6.31, N 4.56. Calc. for $C_{13}H_{17}O_6N$: C 55.12, H 6.05, N 4.94%). δ_H (60 MHz, CD_3COCD_3): 10.90 (1H, deuterium exchangeable, br, NH), 8.55 (1H, d, *J* 12, C6-H), 3.80 (12H, s, 4 OCH_3), 3.25 (3H, d, *J* 4, N-CH_3). $\bar{\nu}_{max}$/cm^{-1} (KBr): 1695 ($\nu_{C=O}$ C4-COOCH$_3$), 1640 ($\nu_{C=O}$ C1-COOCH$_3$). MS, *m/z* 284 (17%) (M + 1), 283 (75) (M), 268 (15), 251 (40), 236 (100), 221 (46), 162 (13), 42 (12). UV, λ_{max}/nm (log ε) (CH_3CN): 232 (4.3), 400 (4.2).

Dimethyl 6-(2-hydroxy-1-methylethylamino)-2,3-dimethoxyfulvene-1,4-dicarboxylate 6d. Obtained as an oil (Yield 89%) (Found: C 55.20, H 6.60, N 4.19. Calc. for $C_{15}H_{21}O_7N$: C 55.04, H 6.47, N 4.28%). δ_H (60 MHz, CD_3COCD_3): 11.00 (1H, deuterium exchangeable, br, NH), 8.50 (1H, d, *J* 14, C6-H), 3.65 (12H, s, 4 OCH_3), 3.5 (3H, m, $CHCH_2$), 1.15 (3H, d, *J* 7, CH_3). $\bar{\nu}_{max}$/cm^{-1} (film): 3650–2900 ($\nu_{O\text{-}H}$), 1685 ($\nu_{C=O}$ C4-COOCH$_3$), 1635 ($\nu_{C=O}$ C1-COOCH$_3$).

Dimethyl 6-[4-(*N*,*N*-dimethylamino)anilino]-2,3-dimethoxyfulvene-1,4-dicarboxylate 6e. Mp 148–149 °C (yield 70%) (Found: C 61.51, H 6.20, N 7.03. Calc. for $C_{20}H_{24}O_6N_2$: C 61.84, H 6.23, N 7.21%). δ_H (60 MHz, CD_3COCD_3): 12.90 (1H, deuterium exchangeable, br, NH), 9.1 (1H, d, *J* 14, C6-H), 7.2–6.7 (4H, m, 4 CH ar), 3.8 (12H, s, 4 OCH_3), 2.9 (6H, s, NCH_3). δ_C (50.3 MHz, $CDCl_3$): 168.2 (*C*OOCH$_3$), 165.3 (*C*OOCH$_3$), 154.1 and 149.5 (C2 and C3), 147.1 (C4 ar), 143.6 (C6), 130.9 (C1 ar), 128.5 (C2 ar), 114.5 (C3 ar), 112.7 (C4), 107.0 (C5), 105.6 (C1), 61.6 (OCH_3), 61.3 (OCH_3), 52.0 (COO*C*H$_3$), 51.3 (COO*C*H$_3$), 41.4 [$N(CH_3)_2$]. $\bar{\nu}_{max}$/cm^{-1} (film evaporated from $CHCl_3$): 1690 ($\nu_{C=O}$ C4-COOCH$_3$), 1625 ($\nu_{C=O}$ C1-COOCH$_3$). MS, *m/z* 388 (16%) (M), 356 (16), 341 (31), 178 (20), 167 (34), 122 (32), 105 (16), 91 (24), 77 (26), 69 (100), 59 (24), 44 (30), 41 (35). UV λ_{max}/nm (log ε) (CH_3CN): 241 (4.5), 282 (4.1), 330 (3.9), 470 (4.5).

Dimethyl (*S*)-6-[4-(2-hydroxymethylpyrrolidin-1-yl]anilino)-2,3-dimethoxyfulvene-1,4-dicarboxylate 6g. Oil (yield 57%). (Found: C 62.07, H 6.28, N 6.25. Calc. for $C_{23}H_{28}O_7N_2$: C 62.15, H 6.35, N 6.30%). δ_H (300 MHz, $CDCl_3$): 13.13 (1H, deuterium exchangeable, d, *J* 14, NH), 9.25 (1H, d, *J* 14, C6-H), 7.20–6.68 (4H, m, C_6H_4), 3.95 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.88–3.85 (1H, m, NCH), 3.70–3.63 (2H, m, CH_2OH), 3.52–3.49 (1H, m, NCH_aH_b), 3.19–3.15 (1H, m, NCH_aH_b), 2.07–2.02 (4H, m, $NCH_2CH_2CH_2$). δ_C (75.5 MHz, $CDCl_3$): 168.3 (*C*OOCH$_3$), 165.4 (*C*OOCH$_3$), 153.5 and 149.1 (C2 and C3), 146.0 (C4 ar), 144.0 (C6), 129.3 (C1 ar), 118.8 (C2 ar), 113.1 (C3 ar), 106.9 (C5), 105.5 (C1), 112.6 (C4), 63.6 (CH_2OH), 61.7 (OCH_3), 61.5 (OCH_3), 60.3 (N-CH), 52.1 (COO*C*H$_3$), 51.3 (COO*C*H$_3$), 49.6 (N-CH_2), 28.7 (NCH$_2$CH$_2$*C*H$_2$), 23.7 (N-CH$_2$-*C*H$_2$-CH$_2$). $\bar{\nu}_{max}$/cm^{-1} (film evaporated from $CHCl_3$): 3500–2500 ($\nu_{O\text{-}H}$), 1705 ($\nu_{C=O}$C4-COOCH$_3$), 1645 ($\nu_{C=O}$ C1-COOCH$_3$). MS, *m/z*: 445 (10%) (M + 1), 444 (32) (M), 413 (17), 382 (25), 381 (100), 351 (18), 43 (10). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 244 (3.3), 288 (2.9), 341 (2.9), 481 (3.4).

Dimethyl (*R*)-6-[4-(1-cyclohexylethylamino)anilino]-2,3-dimethoxyfulvene-1,4-dicarboxylate 6h. Oil (yield 83%) (Found: C 66.58, H 7.43, N 5.90. Calc. for $C_{26}H_{34}O_6N_2$: C 66.36, H 7.28, N 5.95%). δ_H (300 MHz, $CDCl_3$): 13.12 (1H, deuterium exchangeable, d, *J* 14, NH), 9.24 (1H, d, *J* 14, C6-H), 7.13–6.54 (4H, m, C_6H_4), 3.94 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.35–3.20 (1H, m, NCH), 1.86–0.92 (11H, m, cyclohexyl-H), 1.12 (3H, d, *J* 6, CH_3). δ_C (75.5 MHz, $CDCl_3$): 168.3 ($COOCH_3$), 165.5 ($COOCH_3$), 153.5 and 149.0 (C2 and C3), 146.0 (C4 ar), 144.0 (C6), 129.4 (C1 ar), 119.1 (C2 ar), 113.7 (C3 ar), 106.9 (C5), 105.5 (C1), 112.6 (C4), 61.7 (OCH_3), 61.5 (OCH_3), 53.3 (N-CH), 52.1 ($COOCH_3$), 51.3 ($COOCH_3$), 43.0, 29.7, 28.4, 26.6, 26.4, 26.3 (cyclohexyl-C), 17.4 (CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3390 ($\nu_{N\text{-}H}$), 1695 ($\nu_{C=O}$ C4-$COOCH_3$), 1630 ($\nu_{C=O}$ C1-$COOCH_3$). MS, *m/z*: 471 (11) (M+1), 470 (36%) (M), 438 (20), 355 (100), 325 (13). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 269 (3.8), 342 (3.1), 477 (3.6).

Synthesis of methyl 6-amino-4-cyano-2,3-dimethoxyfulvene-1-carboxylates 7

General procedure

An equimolar mixture of 100 mg (0.40 mmol) of methyl 4-cyano-2,3,6-trimethoxyfulvene-1-carboxylate and the appropriate amine in 20–50 ml of methylene chloride was stirred at room temp. for 30–90 min (depending on the amine, reaction monitored by TLC). The solvent was then removed under reduced pressure and the compound was chromatographed on silica gel using methylene chloride as eluent.

Methyl 6-anilino-4-cyano-2,3-dimethoxyfulvene-1-carboxylate 7a. Mp 148–149 °C (yield 73%) (Found: C 65.52, H 5.41, N 8.68. Calc. for $C_{17}H_{16}O_4N_2$: C 65.38, H 5.16, N 8.97%). δ_H (80 MHz, $CDCl_3$): 12.42 (1H, d deuterium exchangeable, d, *J* 13, NH), 7.85 (1H, d, *J* 13.1, C6-H), 7.60–7.04 (4H, m, 4 CH ar), 4.19 (3H, s, C3-OCH_3), 3.95, 3.93 (6H, 2s, C2-OCH_3, $COOCH_3$). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 2215 (ν_{CN}), 1660 ($\nu_{C=O}$). MS, *m/z* 312 (82%) (M), 281 (13), 280 (60), 266 (42), 265 (100), 222 (13), 223 (15), 166 (10), 91 (17). UV, λ_{max}/nm (log ε) (CH_3CN): 244 (4.2), 434 (4.5).

Methyl 6-anisidino-4-cyano-2,3-dimethoxyfulvene-1-carboxylate 7b. Mp 97–98 °C (yield 85%) (Found: C 68.50, H 6.60, N 7.58. Calc. for $C_{21}H_{24}O_4N_2$: C 68.46, H 6.57, N 7.60%). δ_H (80 MHz, $CDCl_3$): 12.47 (1H, deuterium exchangeable, d, *J* 13, NH), 7.79 (1H, d, *J* 13.3, C6-H), 7.23–6.85 (4H, m, 4 CH ar.), 4.17 (3H, s, C3-OCH_3), 3.93 (6H, s, C2-OCH_3, $COOCH_3$). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated of $CHCl_3$): 2210 (ν_{CN}), 1655 ($\nu_{C=O}$). MS, *m/z* 368 (100%) (M), 337 (11), 336 (46) (M−32), 322 (10), 321 (38), 308 (19), 307 (76). UV, λ_{max}/nm) (log ε) (CH_3CN): 232 (4.28), 443 (4.45).

Methyl 6-butylamino-4-cyano-2,3-dimethoxyfulvene-1-carboxylate 7c. Mp 60–61 °C (yield 96%) (Found: C 61.64, H 6.94, N 9.19. Calc. for $C_{15}H_{20}O_4N_2$: C 61.63, H 6.70, N 9.58%). δ_H (80 MHz, $CDCl_3$): 10.70 (1H, deuterium exchangeable, br, NH), 7.41 (1H, d, *J* 14, C6-H), 4.10 (3H, s, C3-OCH_3), 3.88 (6H, s, C2-OCH_3, $COOCH_3$), 3.45 (2H, m, CH_2N), 1.90–0.97 (7H, m, $CH_2CH_2CH_3$). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 2200 (ν_{CN}),1660 ($\nu_{C=O}$). MS, *m/z* 292 (100%) (M), 277 (47), 260 (21), 245 (38), 217 (52), 203 (52), 189 (22), 174 (14), 146 (11). UV, λ_{max}/nm (log ε) (CH_3CN): 225 (4.2), 399 (4.2).

Methyl 4-cyano-6-(2-hydroxy-1-methylethylamino)-2,3-dimethoxyfulvene-1-carboxylate 7d. Mp 95–96 °C (yield 82%) (Found: C 57.33, H 6.34, N 9.36. Calc. for $C_{14}H_{18}O_5N_2$: C 57.14, H 6.16, N 9.52%. δ_H (80 MHz, $CDCl_3$): 10.65 (1H, deuterium exchangeable, br, NH), 7.49 (1H, d, *J* 14, C6-H), 4.09 (3H, s, C3-OCH_3), 3.87 (6H, s, C2-OCH_3, $COOCH_3$), 3.65 (3H, m, $CHCH_2$), 1.35 (3H, d, *J* 6, CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 2200 (ν_{CN}), 1645 ($\nu_{C=O}$). UV, λ_{max}/nm (log ε) (CH_3CN): 226 (4.3), 400 (4.4).

Synthesis of 6-amino-2,3-dimethoxyfulvene-1,4-dicarbonitriles 9

General procedure

To a solution of 100 mg (0.46 mmol) of 6-hydroxy-2,3-dimethoxyfulvene-1,4-dicarbonitrile in 15 ml of methylene chloride, an equimolar amount of the appropriate amine was added. The mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and finally the residue was chromatographed on silica gel (eluent, AcOEt–hexane, 1 : 4) to give the corresponding amino compound.

(*S*)-6-[4-(2-Hydroxymethylpyrrolidin-1-yl)anilino)]-2,3-dimethoxyfulvene-1,4-dicarbonitrile 9g. Mp 105 °C (yield 89%) (Found: C 66.71, H 5.80, N 14.60. Calc. for $C_{21}H_{22}O_3N_4$: C 66.65, H 5.86, N 14.80%). δ_H (300 MHz, $CDCl_3$): 8.30 (1H, deuterium exchangeable, d, *J* 14, NH), 7.48 (1H, d, *J* 14, C6-H), 7.03–6.66 (4H, m, C_6H_4), 4.22 (3H, s, OCH_3), 4.18 (3H, s, OCH_3), 3.92–3.78 (1H, m, NCH), 3.72–3.58 (2H, m, CH_2OH), 3.55–3.45 (1H, m, NCH_aH_b), 3.20–3.08 (1H, m, NCH_aH_b), 2.10–1.95 (4H, m, $NCH_2CH_2CH_2$). δ_C (75.5 MHz, $CDCl_3$): 154.1 and 150.6 (C2 and C3), 146.0 (C4 ar), 135.9 (C6), 128.6 (C1 ar), 118.7 (CN), 118.5 (C2 ar), 115.0 (CN), 113.1 (C3 ar), 107.4 (C5), 85.5 (C4), 76.7 (C1), 63.6 (CH_2OH), 60.3 (NCH), 59.5 (2 OCH_3), 49.6 (N-CH_2), 28.7 ($NCH_2CH_2CH_2$), 23.7 ($NCH_2CH_2CH_2$). $\bar{\nu}_{max}/cm^{-1}$ (KBr): 3500–2500 ($\nu_{O\text{-}H}$), 2190 (ν_{CN}). MS, *m/z* 378 (33%) (M), 348 (24), 347 (100), 317 (13). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 265 (3.9), 338 (3.8), 467 (4.3).

(*R*)-6-[4-(1-Cyclohexylethylamino)anilino]-2,3-dimethoxyfulvene-1,4-dicarbonitrile 9h. Mp 110 °C (yield 94%) (Found: C 71.60, H 7.09, N 13.76. Calc. for $C_{24}H_{28}O_2N_4$: C 71.26, H 6.98, N 13.85%). δ_H (300 MHz, $CDCl_3$): 8.28 (1H, deuterium exchangeable, d, *J* 14, NH), 7.48 (1H, d, *J* 14, C6-H), 6.98–6.52 (4H, m, C_6H_4), 4.23 (3H, s, OCH_3), 4.18 (3H, s, OCH_3), 3.35–3.20 (1H, m, N-CH), 1.86–0.92 (11H, m, cyclohexyl-H), 1.12 (3H, d, *J* 6, CH_3). δ_C (75.5 MHz, $CDCl_3$): 154.0 and 150.5 (C2 and C3), 146.0 (C4 ar), 136.2 (C6), 129.7 (C1 ar), 118.7 (C2 ar, CN), 115.0 (CN), 113.8 (C3 ar), 107.2 (C5), 76.6 (C1), 85.5 (C4), 61.7 (OCH_3), 59.5 (2 OCH_3), 53.3 (NCH), 43.0, 29.7, 28.4, 26.6, 26.4, 26.3 (cyclohexyl-C), 17.4 (CH_3). $\bar{\nu}_{max}/cm^{-1}$ (film evaporated from $CHCl_3$): 3380 ($\nu_{N\text{-}H}$), 2190 (ν_{CN}). MS, *m/z* 405 (10%) (M+1), 404 (39%) (M), 322 (21), 321 (100). UV, λ_{max}/nm (log ε) (CH_2Cl_2): 259 (4.0), 338 (3.9), 462 (4.3).

X-Ray diffraction

Suitable crystals were grown from an AcOEt–hexane (1:2) solution for **6b**, and from an acetone solution for **6c** and **6e**. Cell constants were obtained by least-squares refinement on diffractometer angles for 25 automatically centred reflections. Data were obtained at room temperature using a CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), $1 < \theta < 25°$. Lorentz–polarization, but not absorption, corrections were applied. Structures were solved by direct methods (SHELXS-86[12]) and refined by full-matrix least-squares on F^2 for all reflections (SHELXL-93[13]). Geometrical calculations were carried out using the program PARST-95.[14]

Crystal data and structure determination details are shown in Table 1. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/72.

Table 1 Crystal data and structure determination details of **6b**, **6c** and **6e**

compound	**6b**	**6c**	**6e**
formula	$C_{19}H_{21}NO_7$	$C_{13}H_{17}NO_6$	$C_{20}H_{24}N_2O_6$
M	375.37	283.28	388.41
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	*Pcab*	*C*2/*c*	*Pbca*
a/Å	12.895(4)	7.985 (1)	7.479(2)
b/Å	15.092(2)	14.598 (1)	12.575(1)
c/Å	18.958(3)	12.325 (5)	41.675(4)
β/°	90	103.85 (2)	90
V/Å^3	3689(1)	1394.9(6)	3919(1)
Z	8	4	8
D_{calc}/g cm^{-3}	1.352	1.349	1.316
μ/mm^{-1}	0.10	0.11	0.10
F(000)	1584	600	1648
Crystal size/mm	0.30 × 0.25 × 0.25	0.36 × 0.30 × 0.16	0.40 × 0.32 × 0.21
h, k, l range	0/15, 0/17, 0/22	−11/10, 0/20, 0/17	0/8, 0/14, 0/49
Unique reflections	3184	2039	3450
Parameters	277	114	331
$R[F]$[a] [for $I_o > 2\sigma(I_o)$]	0.044 (1758)	0.042 (1080)	0.032(1459)
$R_w[F^2]$[b] (for all refl.)	0.120	0.162	0.091
Weighting parameters[c]	$a=0.078$, $b=0$	$a=0.089$, $b=0.009$	$a=0.054$, $b=0$
Max., min. electron density/e Å^{-3}	0.20, −0.13	0.17, −0.17	0.17, −0.11

[a] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w(F^2)=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$. [c] $w^{-1}=[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=[\max(F_o^2,0)+2F_c^2]/3$.

Results and Discussion

EFISH experiments

Experimental values for the third-order EFISH polarizabilities $\gamma(-2\omega{:}\omega,\omega,0)$, ground state dipole moment μ and the component $\beta_{zzz}(2\omega)$ of the β tensor are reported in Table 2.

In the 6-aminofulvene group, the highest β values are observed for **4b**, **6b** and **6e**. These values can be understood as arising from a charge-transfer transition between the donor group attached to the benzenic ring and the nitrogen joined to the fulvene acting as an acceptor. Consequently, β increases with the donor character of the group attached to the benzene. It is interesting to remember here the $\beta(0)$ of *p*-*N*,*N*-dimethylnitroaniline, 10×10^{-30} esu, in relation to the $\beta(0)$ of **6e**, 15×10^{-30} esu.

The low solubility of 6-aminofulvenes **5** has hindered the β measurements. Only for **5a** has β been determined. The β_{zzz} values of 6-aminopentafulvenes **7** are practically zero, even in the case of **7b**, where the fragment MeO—C$_6$H$_4$—NH—R is present. These results could imply a small β value for these molecules but this idea does not seem consistent with the rest of the results for the 6-aminofulvenes. The β value for **7b** is small but not zero and the replacement of OH by OMe does not cancel out β in the case of **4** (comparison between **4** and **6**). So, the zero β_{zzz} values for **7** rather suggest that the angle between the dipole moment and β vector is close to 90° in these molecules leading to a $\mu\beta_{zzz}$ product of practically zero. The different relative orientations of μ and β vectors can be attributed mainly to different conformations. It is known that the value and the direction of the dipole moment depend strongly on the conformation in the case of highly functionalized fulvenes.[15]

Table 2 Linear optical spectroscopic and nonlinear optical properties of fulvenes at $\lambda=1.34$ µm: Transition wavelength (λ_{max}), third-order polarizability (γ^{EFISH}), ground state dipole moment (μ), $\beta_{zzz}(2\omega)$ component [$\beta(2\omega)$] and static β_{zzz} value [$\beta(0)$] calculated assuming a two level model

compound	λ_{max}/ nm	γ^{EFISH}/ 10^{34} esu	μ/ Debyes	$\beta(2\omega)$/ 10^{30} esu	$\beta(0)$/ 10^{30} esu
4a	452	1.0	6.2	2.5	1.2
4b	460	5.5	6.5	9.1	4.2
4d	440	0	4.4	0	0
5a	440	1.2	5.5[b]	4.4	2.2
6a	448	0.7	4.1	3.3	1.6
6b	452	2.1	3.5	12.1	5.8
6c	410	0.3	3.6	1.9	1.1
6e	478	7.7	4.6	34.7	14.9
7a	*a*	0	6.1	0	0
7b	*a*	0	5.9	0	0
7c	*a*	0	6.1	0	0
7d	*a*	0	6.9	0	0
8a	465	8.0	8.8	18.8	8.6
8b	455	−4.2	8.6	−10.2	−4.9
8c	468	−3.7	4.2	−18.5	−8.3

[a] UV spectra cited in this table have recorded in CHCl$_3$. For 7a–d spectra in this solvent have not been measured. Spectra recorded in CH$_3$CN are described in the Experimental section. [b] Calculated value.

The electronic distribution in 6-azafulvenes **8** is different from that in fulvenes. Compounds **8** can be considered as cyclopentadienone phenylhydrazones and are polyolefinic.[6] They show fair β_{zzz} values and the structural dependence of β_{zzz} is different from that described for fulvenes **6**. In this case, β_{zzz} becomes more positive as the *para* substituent of benzene is more charge-withdrawing. The sign of β, which is related to the change in dipole moment from the ground to the relevant excited state, $\Delta\mu=\mu_e-\mu$, changes from positive in **8a** to negative in **8b** and **8c**. This change could be related to two opposite contributions to the dipole moment. The aminic N can donate its electrons to the 6-azafulvene moiety or to the benzene moiety. The second contribution is more important when a strong withdrawing group is attached to the benzene, *e.g.* NO$_2$ (**8a**).

For a more correct assessment of the results it would be more relevant to report the static β values (at zero frequency). For such purpose, a quantum-mechanical microscopic model describing the dispersive behaviour of β needs to be implemented. A two-level model, traditionally used in dipolar systems,[1] may be used in this case, by assuming that the low energy transition, associated with charge transfer (CT) between the donor and the acceptor group, dominates the nonlinear response. Therefore, the static $\beta(0)$ values for all the compounds have been calculated (see Table 2) through the expression in eqn. (1),

$$\beta(-2\omega)=\frac{3fe^2\Delta\mu}{2m^2\hbar}\,\frac{\omega_{01}}{(\omega_{01}{}^2-4\omega^2)(\omega_{01}{}^2-\omega^2)}$$
$$=\beta(0)\,\frac{\omega_{01}{}^4}{(\omega_{01}{}^2-4\omega^2)(\omega_{01}{}^2-\omega^2)} \qquad (1)$$

where f is the oscillator strength of the CT transition, $\Delta\mu$ is the dipole moment difference between the excited and ground state, ω and ω_{01} are respectively the frequency of the fundamental beam and that of the excited state, e and m are respectively the charge and mass of the electron and $\hbar$ is Planck's constant.

From Table 2, it may be seen that the previous discussion for the experimental β values remains valid at zero frequency. This ensures that the β variations observed with the different donor (attracting) character of the substituents are intrinsically related to the modification of the chemical structure and not to resonance contributions.

X-Ray structure determination

X-Ray diffraction studies were carried out on the two compounds of highest β value (**6b** and **6e**) and on **6c** with a similar structure and a smaller β value.

All of them show a similar structural disorder in the solid state (Fig. 1). In **6c**, the site occupation factor of the two molecules is 0.5 and the average molecule is symmetric, that is, the asymmetric unit is half a molecule (Fig. 1). The ratio for the two molecules occupying the same crystallographic site is 0.81/0.19 in compound **6b** and 0.66/0.34 in **6e**. In both structures the disorder affects mainly C6, N61 and the benzenic group. All these atoms have been split in the refined model. The distance between split peaks decreases as they are far away from the fulvenic ring and, in fact, the phenyl group substituent (MeO or MeN_2) has been refined without splitting.

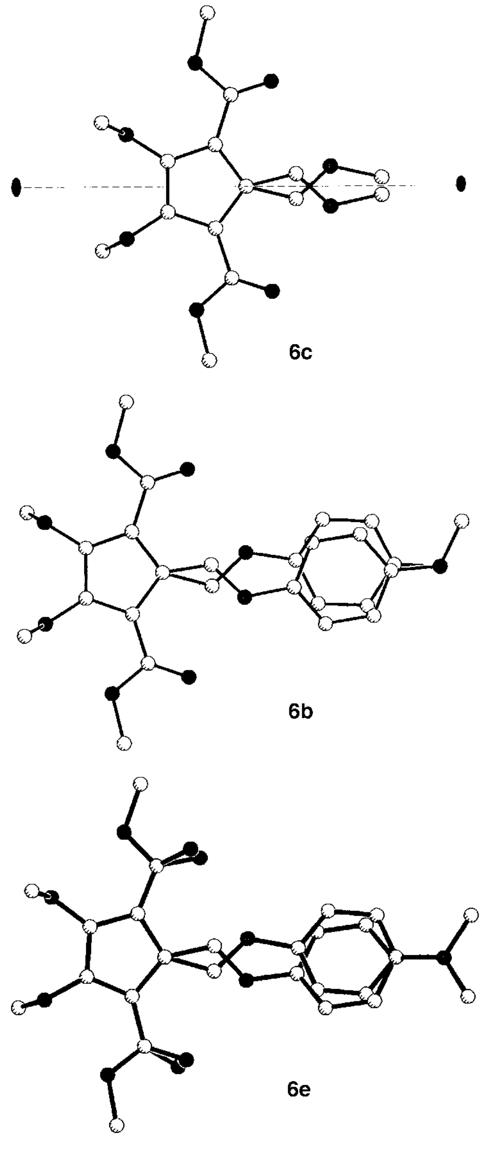


Fig. 1 Structural disorder found in solid state for compounds **6b**, **6c** and **6e** (PLUTON[17]). In the case of **6c**, the crystallographic twofold axis is shown.

Table 3 summarizes selected bond lengths of these three structures. They show no significant differences. The bond length alternation is smaller than that found in fulvenes, mainly polyolefinic, pointing to the presence of a considerable cyclic conjugation in the five-membered ring (for an exhaustive analysis of fulvenic ring distances see ref. 16). In contrast, 6-azafulvenes **8** present a clear bond alternation and their structure is mainly polyolefinic.[6]

The N-atom attached to C6 adopts a planar trigonal disposition. In **6b** and **6e** the distance N–fulvene is considerably shorter than the N–benzene one, which implies that the electronic charge of N is mainly directed to the fulvene. The electron donation from N to fulvene also induces lengthening of the exocyclic bond C5—C6. This result supports the explanation given for the high β values for these two compounds. Moreover, the fact that **6c**, having a molecular structure similar to **6b** and **6e**, shows a small β value is in accordance with the idea that a benzene supporting a donor group is a requirement for having a high β value in this kind of compound.

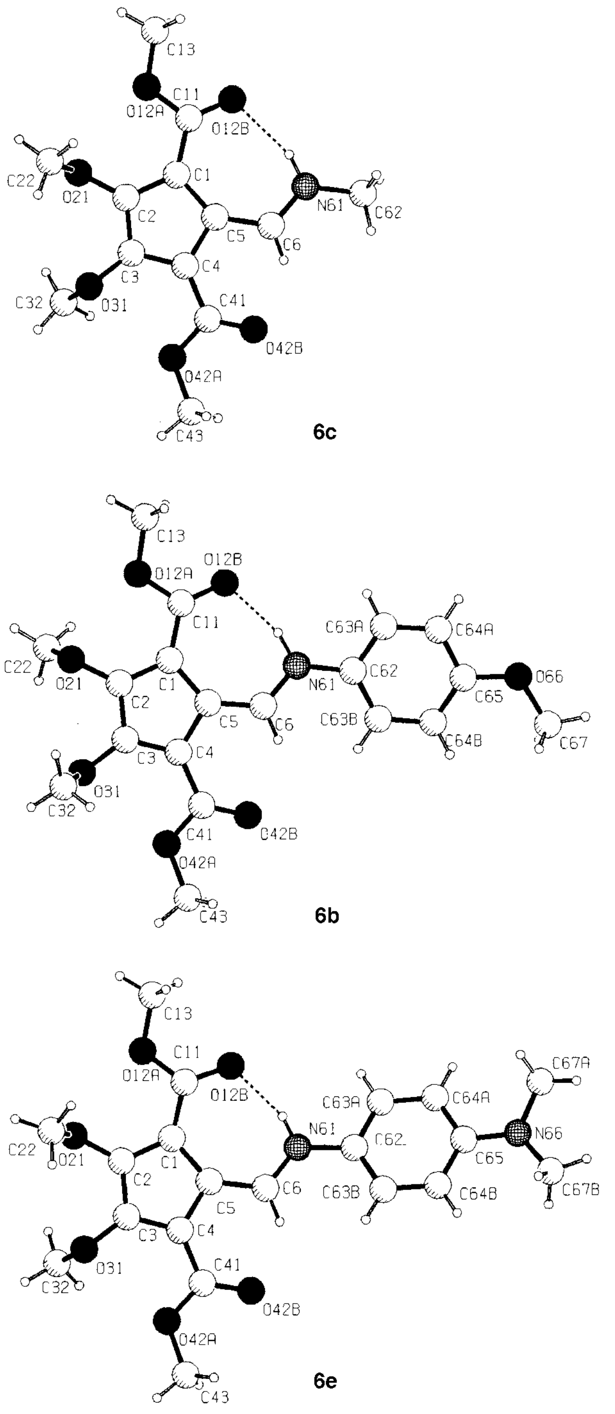
The fulvenic backbone is practically planar: the atomic deviations from the C1—C2—C3—C4—C5—C6 mean plane are less than 0.01 in **6c**, 0.03 in **6b** and 0.04 Å in **6e**. The ester atoms are located near to the ring plane: the dihedral angles between the C—COO mean plane and the ring mean plane are small [range 1.7(1)°–12.2(1)°]. In contrast, the methoxy groups are disposed in planes almost perpendicular to the ring: the dihedral angles between the C—O—C mean plane and the ring mean plane are in the range 78.8(1)°–88.1(1)° (Fig. 2). In every molecule, the two methoxy groups are placed on opposite sides and the two ester groups are disposed in such a way that the carbonyl groups point in the same direction (parallel disposition). In a previously described dimethyl 6-aminofulvene-1,4-dicarboxylate, the two ester groups are also coplanar, but carbonyl groups point in opposite directions (antiparallel disposition).[4]

The benzene ring in **6b** and **6e** is twisted and tilted in relation to the fulvene ring: the dihedral angles between their respective planes are 10.5(1)° for **6b** and 24.4(1)° for **6e**. An interesting feature in these compounds is the presence of an

Table 3 Selected bond lengths of **6b**, **6c** and **6e** (esd in parentheses)

length/Å	**6b**	**6c**[a]	**6e**
C1—C11	1.455(3)	1.459(2)	1.454(3)
C11—O12B	1.217(2)	1.211(2)	1.239(5)
C11—O12A	1.332(3)	1.332(2)	1.320(2)
O12A—C13	1.441(3)	1.437(2)	1.448(2)
C1—C2	1.386(3)	1.391(2)	1.390(2)
C2—O21	1.359(2)	1.364(2)	1.367(2)
O21—C22	1.407(3)	1.417(2)	1.410(2)
C2—C3	1.414(3)	1.409(3)	1.406(2)
C1—C5	1.444(3)	1.443(2)	1.443(3)
C5—C6	1.389(4)	1.423(3)	1.441(3)
C6—N61	1.315(4)	1.314(3)	1.320(3)
N61—C62	1.416(3)	1.451(4)	1.442(3)
C4—C41	1.458(3)	1.459(2)	1.451(3)
C41—O42B	1.190(3)	1.211(2)	1.240(7)
C41—O42A	1.311(3)	1.332(2)	1.321(2)
O42A—C43	1.442(3)	1.437(2)	1.440(2)
C3—C4	1.380(3)	1.391(2)	1.385(2)
C3—O31	1.366(2)	1.364(2)	1.367(2)
O31—C32	1.411(3)	1.417(2)	1.412(2)
C4—C5	1.444(3)	1.443(2)	1.439(3)

[a] The asymmetric unit is half a molecule.



6c

6b

6e

Fig. 2 Drawings of molecular structure for **6b**, **6c** and **6e** determined by single crystal X-ray diffraction. Intramolecular H-bondings are indicated by dotted lines (PLUTON[17]).

intramolecular H-bond, forming a seven-membered ring (Table 4). This H-bonding stabilizes the enaminic form and the fulvenic structure therefore also contributes to the planarity of the system. It causes the aminic H deshielding and the corresponding signal in ^{1}H NMR is observed at δ 10.9 for **6c** and δ 12.9–13.0 for **6b** and **6e**. Moreover, vicinal couplings H$-$N$-$C6$-$H are detected. In IR, the ester C$=$O vibration is decreased to 1635–1655 cm^{-1}.

Finally, it must be pointed out that the structures of these three compounds are centrosymmetric and therefore, even though **6b** and **6e** show moderate β values, they do not have macroscopic second order optical properties.

Table 4 Intramolecular H-bonding geometry[a]

compound	d(O12B···H)/ Å	d(N61···O12B)/ Å	<(N61$-$H···O12B) (°)
6c	1.91	2.900(3)	160
6b[b]	1.75	2.745(3)	161
6e[b]	1.71	2.666(6)	153

[a]The N$-$H bonding has been normalized to 1.03 Å. [b]The reported values correspond to the main component of disorder.

Table 5 Estimated d_{eff} values of 6-anilinopentafulvenes determined by the SHEW techique compared with *m*-nitroaniline

compound	**4g**	**5g**	**9g**	**9h**
d_{eff}/pm^{-1} V	0	170	6.7	12

SHEW measurements

From EFISH experiments, in highly functionalized 6-aminofulvenes the highest β values seem to be related to the presence of a benzenic ring with a donor group attached in the *para* position. On the other hand, a SHG active material has to have a non-centrosymmetric structure. We have satisfied these two requirements by synthesizing 6-aminofulvenes derived from chiral *p*-phenylenediamines. In this way we obtain 6-anilinofulvenes with a donor amino group bonded to the benzenic ring; the chirality implies a non-centrosymmetric structure.

Two *p*-phenylenediamines have been considered and synthesized. One of them, **10g**, includes a tertiary amine whereas **10h** incorporates a secondary amine. Both of them have been obtained by reduction of the corresponding *p*-nitroanilines **11g** and **11h**, **11g** being a well known organic NLO compound, NPP.[11] In contrast, product **11h** is new. Its SHG activity has been determined in this work by the SHEW technique, its d_{eff} being only 0.47 times that of *m*-nitroaniline [the d_{eff} for **11g** (NPP) is 4.3 times that for *m*-nitroaniline]. Eight chiral 6-anilinofulvenes, **4g–h**, **5g–h, 6g–h** and **9g–h**, have been synthesized from the corresponding 2,3,6-trioxyfulvenes and the two *p*-phenylenediamines, **10g–h**. Four of them, **4h, 5h, 6g–h**, are oils. For the rest, the d_{eff} value has been measured (Table 5). The 6-anilinofulvene **5g** has a fairly large d_{eff} and becomes an interesting new NLO organic compound.

Conclusions

Several new fulvenes, with a fair hyperpolarizability, have been synthesized. In these compounds, the fulvenic ring shows an appreciable cyclic conjugation whereas in related 6-azafulvenes, a polyolefinic structure has been determined. Consequently, differences have been also observed in the structural dependence of the measured β values. In the new fulvenes the highest β values are associated with the presence in the molecule of a benzenic ring having a donor group in the *para*-position. Following this idea some chiral 6-anilinofulvenes have been synthesized, one of them shows a fairly large d_{eff}.

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