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Photochemical dimerisation of 2-vinylfuran and 2-vinylthiophene derivatives bearing electron-withdrawing groups

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Abstract

The photochemical dimerisation of 1,3-diheteroaryl-2-propen-1-one derivatives gave a mixture of dimers in agreement with the hypothesis that the reaction is under frontier orbitals control and preferential formation of only the more stable isomers. On the contrary, the reaction of 2-heteroaryl-nitroethylene derivatives were not observed to give cyclobutane dimers but only coupling products with the loss of one nitro group. This behaviour is in agreement with the nature of the HOMO–LUMO orbitals which do not allow the superimposition of the reagents. This result allows to formulate the hypothesis that the photochemical dimerisation of 1-heteroaryl-2-EWG-ethylenes must occur as a concerted reaction. Finally, 2-heteroaryl-1,1-dicyanoethylene derivatives gave the corresponding dimers. Also in this case, we obtained only the head-to-head dimer and the more stable one. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: LUMO-S_0; HOMO-S_0; LSOMO-S_1; HSOMO-T_1; Dimer

1. Introduction

Cycloaddition reaction of alkenes to give cyclobutane dimers is one of the most studied reaction in organic photochemistry [1]. Some years ago we found that the irradiation of methyl 3-(2-furyl)acrylate (**1**) in the presence of benzophenone gave a mixture of two isomeric dimers **2** and **3** (Scheme 1) [2]. Subsequently, we found that this reaction occurs in the triplet state of the molecule and that this triplet state is obtained via energy transfer from benzophenone [3]. The regiochemical behaviour of methyl 3-(2-furyl)acrylate was explained assuming a reaction between the LSOMO of the triplet state of **1** with the LUMO of **1** in its ground state. Furthermore, the stereochemistry observed in the reaction **1** → **2** could be explained assuming the formation of the more stable isomers [4]. On the basis of these results we tested our hypothesis on the reaction mechanism of the dimerisation reaction in solution in the presence of arylacrylonitrile derivatives **4** and of esters of urocanic acid **8** (Scheme 1) [5,6].

In this paper, we want to report our further results on the photochemical dimerisation reaction of furyl and thienyl substituted alkenes bearing electron withdrawing substituents. In particular we describe the dimerisation reactions of 1,3-diheteroaryl-propenones (**10**, Scheme 2), nitroethylene derivatives (**15**, Scheme 3), and 1,1-dicyanoethylene derivatives (**20**, Scheme 4).

2. Materials and methods

Mass spectra were obtained with a Hewlett-Packard 5971 mass-selective detector on a Hewlett-Packard 5890 gas chromatograph (OV-1 capillary column between 70 and 250°C (20°C min^{-1})). NMR spectra were recorded on a Bruker 300 AM instrument. Elemental analyses were obtained by using a Carlo Erba Elemental Analyser 1106. Compounds **10a–d** were obtained through aldol condensation between 2-substituted heterocyclic carboxyaldehydes and heterocyclic methyl ketone derivatives. In particular compound **10a** was prepared following the method reported in [7,8], compounds **10b–d** were prepared on the basis of the procedure of [9]. Compounds **15a–b** were obtained through aldol condensation between 2-substituted heterocyclic carboxylaldehyde and nitromethane [10]. Compounds **20a–b** were prepared via Knoevenagel condensation between the corresponding aldehydes and malononitrile: in particular **20a** was prepared following the procedure described in [11], while **20b** was obtained using the methodology described in [12].

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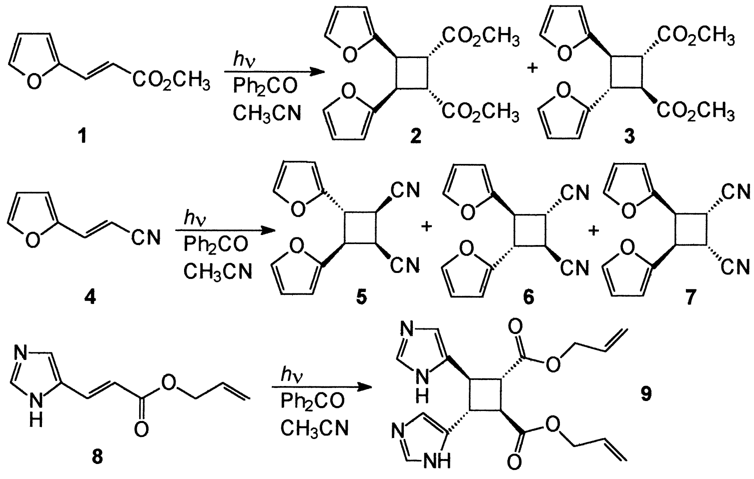
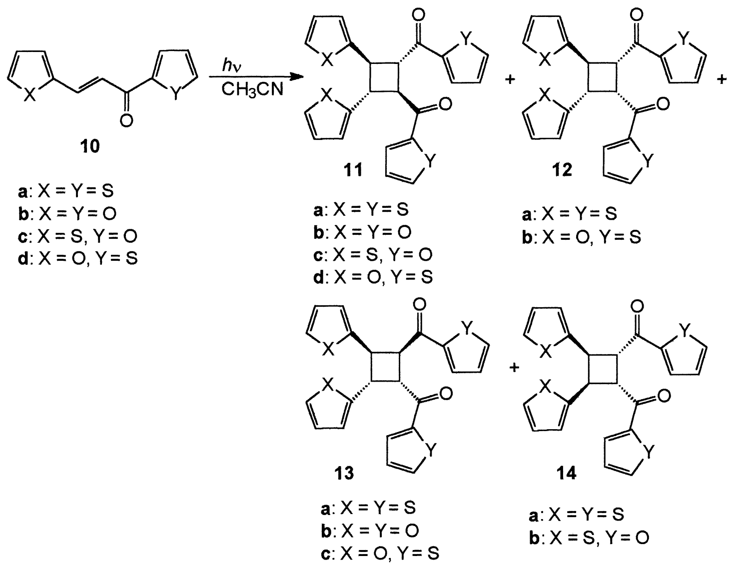
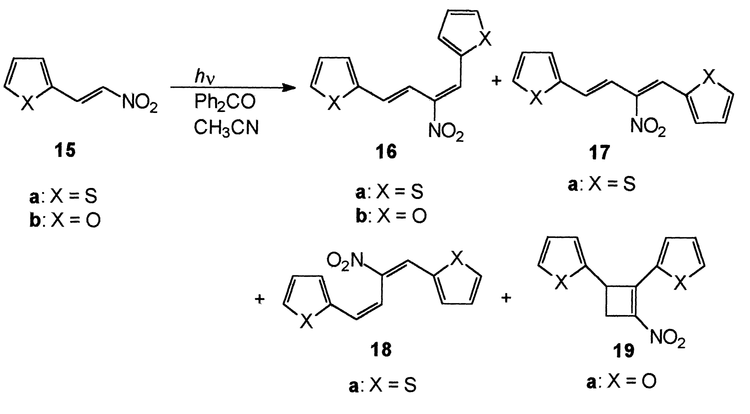


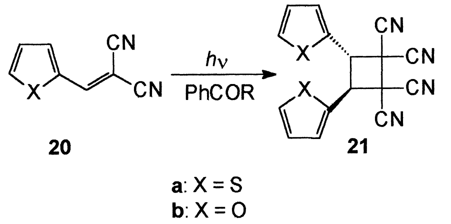
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

The identification of the dimers was performed on the basis of the ^{1}H NMR spectra. The analyses of the ^{1}H NMR spectra of symmetric dimers were performed on the basis of the literature data [13]. In particular, we obtained from the spectra the N, L, K, and M parameters. These values were used to calculate the coupling constant J (J_{AB} in a AA′BB′ system), J' ($J_{AB'}$), J_A ($J_{AA'}$), and J_B ($J_{BB'}$), on the basis of the following equations:

$$K = J_A + J_B$$

$$M = J_A - J_B$$

$$N = J + J'$$

$$L = J - J'$$

2.1. *Irradiation of compounds* **10** *— general procedure*

A solution of compound **10** (3 g) in acetonitrile (100 ml) was flushed with nitrogen for 1 h and then irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz). At the end of the reaction (Table 1) the solvent was evaporated and the crude product was chromatographed on silica gel eluting with *n*-hexane /EtOAc mixtures to give pure products (Table 1).

Table 1
Photochemical dimerisation of 10

Substrate	Irradiation time (h)	Product	Yield (%)
10a	24	**11a**	21
		12a	13
		13a	18
		14a	11
10b	24	**11b**	24
		13b	14
10c	24	**11c**	44
		14b	13
10d	24	**11d**	50
		12b	13
		13c	16

2.2. *r-1,t-2-Di-(2-thienoyl)-c-3,t-4-di-(2-thienyl)cyclobutane (**11a**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.65 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.55 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.23 (dd, 1H, J_1=J_2=3 Hz), 7.02 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.95 (d, 2 H, J=3 Hz), 4.40 (m, 2 H, part of AA′BB′ system: N=9.1 Hz, L=8.8 Hz, K=17 Hz, M=0 Hz), 4.12 ppm (m, 2 H, part of AA′BB′system: N=9.1 Hz, L=8.8 Hz, K=17 Hz, M=0 Hz); MS, *m/z* (relative abundance): 440 (1%), 220 (100), 192 (15). Elemental analysis: found: C 60.03, H 3.59, S 29.00. Calc. for $C_{22}H_{16}O_2S_4$: C 59.97, H 3.66, S 29.11%.

2.3. *r-1,c-2-Di-(2-thienoyl)-c-3,t-4-di-(2-thienyl)cyclobutane (**12a**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 8.11 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.69 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.60 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.14 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.95 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 6.82 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.79 (m, 2 H), 6.73 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 5.22 (dd, 1H, J_1=J_2=9.5 Hz), 4.74 (dd, 1H, J_1=J_2=7 Hz), 4.72 (dd, 1H, J_1=9.5 Hz, J_2=7 Hz), 4.69 ppm (dd, 1H, J_1=9.5 Hz, J_2=7 Hz); MS, *m/z* (relative abundance): 440 (1%), 220 (100), 192 (18). Elemental analysis: found: C 60.05, H 3.71, S 29.02. Calc. for $C_{22}H_{16}O_2S_4$: C 59.97, H 3.66, S 29.11%.

2.4. *r-1,t-2-Di-(2thienoyl)-t-3,c-4-di-(2-thienyl)cyclobutane (**13a**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.86 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.74 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.66 (ddd, 1H, J_1=5 Hz, J_2=4 Hz, J_3=1 Hz), 7.42 (d, 1H, J=5 Hz), 7.15 (m, 2 H), 5.10 (d, 1H, J=4 Hz), 4.98 ppm (d, 1H, J=4 Hz); MS, *m/z* (relative abundance): 440 (2%), 220 (100), 192 (12). Elemental analysis: found: C 59.90, H 3.60, S 29.20. Calc. for $C_{22}H_{16}O_2S_4$: C 59.97, H 3.66, S 29.11%.

2.5. *r-1,c-2-Di-(2-thienoyl)-t-3,t-4-di-(2-thienyl)cyclobutane (**14a**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.59 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.55 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.15 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.02 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.91 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.83 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 4.69 (m, 1H, part of AA′BB′system: N=6.5 Hz, L=6.3 Hz, K=8 Hz, M=0 Hz), 4.65 ppm (m, 1H, part of AA′BB′ system: N=6.5 Hz, L=6.3 Hz, K=8 Hz, M=0 Hz); MS, *m/z* (relative abundance): 440 (3%), 220 (100), 192 (20). Elemental analysis: found: C 59.91, H 3.73, S 29.02. Calc. for $C_{22}H_{16}O_2S_4$: C 59.97, H 3.66, S 29.11%.

2.6. *r-1,t-2-Di-(2-furoyl)-c-3,t-4-di-(2-furyl)cyclobutane (**11b**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.50 (d, 1H, J=2 Hz), 7.38 (dd, 1H, J_1=2 Hz, J_2=1 Hz), 6.99 (d, 1H, J=4 Hz), 6.40 (dd, 1H, J_1=4 Hz, J_2=2 Hz), 6.27 (dd, 1H, J_1=3 Hz, J_2=2 Hz), 6.11 (d, 1H, J=3 Hz), 4.42 (m, 1H, part of

AA′BB′system: N=9.4 Hz, L=9.2 Hz, K=20 Hz, M=0 Hz), 3.99 ppm (m, 1H, part of AA′BB′system: N=9.4 Hz, L=9.2 Hz, K=20 Hz, M=0 Hz); MS, *m/z* (relative abundance): 376 (0.5%), 188 (100), 160 (5). Elemental analysis: found: C 70.10, H 4.21. Calc. for $C_{22}H_{16}O_6$: C 70.21, H 4.28%.

2.7. *r-1,t-2-Di-(2-furoyl)-t-3,c-4-di-(2-furyl)cyclobutane (**13b**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.46 (d, 1H, J=2 Hz), 7.28 (d, 1H, J=4 Hz), 7.10 (d, 1H, J=3 Hz), 6.45 (dd, 1H, J_1=4 Hz, J_2=2 Hz), 6.25 (dd, 1H, J_1=J_2=3 Hz), 6.02 (d, 1H, J=3 Hz), 4.73 (m, 1H, part of AA′BB′system: N=6.1 Hz, L=5.9 Hz, K=24 Hz, M=0 Hz), 4.39 ppm (m, 1H, part of AA′BB′system: N=6.1 Hz, L=5.9 Hz, K=24 Hz, M=0 Hz); MS, *m/z* (relative abundance): 376 (0.7%), 188 (100), 160 (8). Elemental analysis: found: C 70.10, H 4.21. Calc. for $C_{22}H_{16}O_6$: C 70.21, H 4.28%.

2.8. *r-1,t-2-Di-(2-furoyl)-c-3,t-4-di-(2-thienyl)cyclobutane (**11c**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.63 (m, 1H), 7.19 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.09 (d, 1H, J=4 Hz), 6.94 (m, 2 H), 6.42 (dd, 1H, J_1=4 Hz, J_2=2 Hz), 4.28 (m, 1H, part of AA′BB′ system: N=9.4 Hz, L=9.2 Hz, K=17.6 Hz, M=0 Hz), 4.10 ppm (m, 1H, part of AA′BB′ system: N=9.4 Hz, L=9.2 Hz, K=17.6 Hz, M=0 Hz); MS, *m/z* (relative abundance): 408 (0.7%), 204 (100), 192 (6). Elemental analysis: found: C 64.75, H 3.90, S 15.64. Calc. for $C_{22}H_{16}O_4S_2$: C 64.69, H 3.95, S 15.70%.

2.9. *r-1,c-2-Di-(2-furoyl)-t-3,c-4-di-(2-thienyl)cyclobutane (**14b**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.46 (m, 1H), 7.13 (m, 2 H), 6.89 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.83 (d, 1H, J=4 Hz), 6.45 (dd, 1H, J_1=4 Hz, J_2=2 Hz), 4.65 ppm (s, 2 H); MS, *m/z* (relative abundance): 408 (1%), 204 (100), 192 (7). Elemental analysis: found: C 64.73, H 3.87, S 15.66. Calc. for $C_{22}H_{16}O_4S_2$: C 64.69, H 3.95, S 15.70%.

2.10. *r-1,t-2-Di-(2-thienoyl)-c-3,t-4-di-(2-furyl)cyclobutane (**11d**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.62 (ddd, 1H, J_1=4 Hz, J_2=J_3=1 Hz), 7.45 (m, 2 H), 7.00 (ddd, 1H, J_1=J_2=4 Hz, J_3=1 Hz), 6.30 (ddd, 1H, J_1=J_2=4 Hz, J_3=1 Hz), 6.13 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 4.57 (m, 1H, part of AA′BB′ system: N=9.1 Hz, L=8.9 Hz, K=21 Hz, M=0 Hz), 4.02 ppm (m, 1H, part of AA′BB′ system: N=9.1 Hz, L=8.9 Hz, K=21 Hz, M=0 Hz); MS, *m/z* (relative abundance): 408 (0.3%), 204 (100), 160 (3). Elemental analysis: found C 64.64, H 3.90, S 15.73. Calc. for $C_{22}H_{16}O_4S_2$: C 64.69, H 3.95, S 15.70%.

2.11. *r-1,c-2-Di-(2-thienoyl)-c-3,t-4-di-(2-furyl)cyclobutane (**12b**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.96 (dd, 1H, J_1=4 Hz, J_2=1 Hz), 7.68 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.22 (m, 2 H), 7.05 (m, 2 H), 6.20 (dd, 1H, J_1=3 Hz, J_2=2 Hz), 6.05 (dd, 1H, J_1=3 Hz, J_2=2 Hz), 5.99 (d, 1H, J=3 Hz), 5.94 (d, 1H, J=3 Hz), 5.26 (dd, 1H, J_1=J_2=9 Hz), 4.57 (dd, 1H, J_1=J_2=9 Hz), 4.48 (dd, 1H, J_1=J_2=9 Hz), 4.36 ppm (dd, 1H, J_1=J_2=9 Hz); MS, *m/z* (relative abundance): 408 (0.3%), 204 (100), 160 (3). Elemental analysis: found: C 64.64, H 3.90, S 15.73. Calc. for $C_{22}H_{16}O_4S_2$: C 64.69, H 3.95, S 15.70%.

2.12. *r-1,t-2-Di-(2-thienoyl)-t-3,c-4-di-(2-furyl)cyclobutane (**13c**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 7.58 (dd, 1H, J_1=5 Hz, J_2=1 Hz), 7.53 (d, 1H, J=4 Hz), 7.31 (m, 1H), 7.02 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.27 (dd, 1H, J_1=3 Hz, J_2=2 Hz), 6.03 (d, 1H, J=3 Hz), 4.77 (m, 1H, part of AA′BB′ system: N=5.9 Hz, L=5.7 Hz, K=19 Hz, M=0 Hz), 4.42 ppm (m, 1H, part of AA′BB′ system: N=5.9 Hz, L=5.7 Hz, K=19 Hz, M=0 Hz); MS, *m/z* (relative abundance): 408 (0.6%), 204 (100), 160 (3). Elemental analysis: found: C 64.72, H 3.89, S 15.75. Calc. for $C_{22}H_{16}O_4S_2$: C 64.69, H 3.95, S 15.70%.

2.13. *Irradiation of compounds **15** — general procedure*

A solution of compound **15** (3 g) in acetonitrile (100 ml) in the presence of benzophenone (600 mg) was flushed with nitrogen for 1 h and then irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz). At the end of the reaction (Table 3) the solvent was evaporated and the crude product was chromatographed on silica gel eluting with *n*-hexane/EtOAc mixtures to give pure products (Table 3).

2.14. *E,E-1,4-Di-(2-thienyl)-2-nitro-1,3-butadiene (**16a**)*

Viscous oil, ^{1}H NMR (CDCl$_3$) δ: 8.13 (s, 1H), 7.62 (d, 1H, J=5 Hz), 7.48 (dd, 1H, J_1=J_2=4 Hz), 7.44 (d, 1H, J=16 Hz), 7.36 (d, 1H, J=5 Hz), 7.18 (m, 2 H), 7.07 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.90 ppm (d, 1H, J=16 Hz); ^{13}C NMR (CDCl$_3$) δ: 144.8, 141.5, 135.7, 135.4, 132.5, 131.6, 128.7, 128.2, 128.1, 127.0, 126.6 and 114.5 ppm; MS, *m/z* (relative abundance): 265 (5%), 264 (8), 263 (49), 217 (47), 216 (19), 185 (18), 184 (100), 173 (11), 172 (10), 171 (29), 121 (29), 108 (11); IR (CHCl$_3$) $\nu_{\max}$: 3120, 2965, 2915, 2760, 1760, 1630, 1600, 1560, 1520, 1425, 1385, 1310, 1280, 1250, 1220, 1130, 1110, 960, 930, 910, 880, 860, 845 and 825 cm^{-1}. Elemental analysis: found: C 54.69, H 3.48, N 5.38, S, 24.30. Calc. for $C_{12}H_9NO_2S_2$: C 54.73, H 3.44, N 5.32, S 24.35%.

2.15. *Z,E-1,4-Di-(2-thienyl)-2-nitro-1,3-butadiene (**17*a***)*

Viscous oil, ^{1}H NMR ($CDCl_3$) δ: 7.52 (d, 1H, J=5 Hz), 7.29 (dd, 2 H, J_1=J_2=4 Hz), 7.10 (m, 2 H), 7.03 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 6.84 (d, 1H, J=16 Hz), 6.81 (s, 1H), 6.67 ppm (d, 1H, J=16 Hz); ^{13}C NMR ($CDCl_3$) δ: 144.9, 140.8, 134.5, 132.4, 130.7, 128.2, 128.0, 127.9, 126.3, 124.5, 119.3 and 117.9 ppm; MS, *m/z* (relative abundance): 265 (5%), 264 (8), 263 (44), 218 (10), 217 (42), 216 (20), 185 (16), 184 (100), 173 (10), 172 (10), 171 (28), 135 (11), 121 (27), 108 (14). Elemental analysis: found: C 54.69, H 3.48, N 5.38, S, 24.30. Calc. for $C_{12}H_9NO_2S_2$: C 54.73, H 3.44, N 5.32, S 24.35%.

2.16. *E,E-1,4-Di-(2-furyl)-2-nitro-1,3-butadiene (**16*b***)*

Viscous oil, ^{1}H NMR ($CDCl_3$) δ: 7.73 (d, 1H, J=2 Hz), 7.54 (m, 1H), 7.51 (d, 1H, J=16 Hz), 7.50 (m, 1H), 7.19 (d, 1H, J=16 Hz), 6.90 (d, 1H, J=4 Hz), 6.62 (dd, 1H, J_1=4 Hz, J_2=2 Hz), 6.48 ppm (m, 2 H); ^{13}C NMR ($CDCl_3$) δ: 146.8, 145.3, 143.6, 123.2, 119.8, 118.5, 117.9, 114.7, 113.7, 113.2, 112.5 and 112.2 ppm; MS, *m/z* (relative abundance): 232 (9%), 231 (60), 157 (21), 129 (47), 128 (100), 127 (40), 119 (13), 105 (26), 102 (10), 77 (14), 64 (15), 63 (12). Elemental analysis: found: C 62.30, H 3.87, N 6.11. Calc. for $C_{12}H_9NO_4$: C 62.34, H 3.92, N 6.06%.

2.17. *1,4-Di-(2-furyl)-2-nitrocyclobutene (**19*a***)*

Viscous oil, ^{1}H NMR ($CDCl_3$) δ: 7.29 (m, 1H), 7.27 (m, 1H), 6.26 (m, 3 H), 6.03 (dd, 1H, J_1=3 Hz, J_2=1 Hz), 5.74 (dd, 1H, J_1=J_2=9 Hz), 4.53 (dd, 1H, J_1=J_2=9 Hz), 4.18 ppm (dd, 1H, J_1=J_2=9 Hz); ^{13}C NMR ($CDCl_3$) d: 143.0, 142.5, 123.1, 119.8, 113.6, 112.2, 111.6, 111.4, 110.8, 110.5, 108.8, 39.3 and 38.2 ppm; MS, *m/z* (relative abundance): 232 (8%), 231 (51), 157 (23), 129 (43), 128 (100), 127 (42), 119 (18), 105 (25), 96 (10), 90 (10), 77 (15), 64 (16). Elemental analysis: found. C 62.28, H 3.95, N 6.12. Calc. for $C_{12}H_9NO_4$: C 62.34, H 3.92, N 6.06%.

2.18. *Irradiation of compounds **20** — general procedure*

A solution of compound **20** (3 g) in acetonitrile (100 ml) in the presence of benzophenone or acetophenone (600 mg) was flushed with nitrogen for 1 h and then irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz). At the end of the reaction (Table 4) the solvent was evaporated and the crude product was chromatographed on silica gel eluting with *n*-hexane /EtOAc mixtures to give pure products (Table 4).

2.19. *r-1,t-2-Di-(2-thienyl)-3,3,4,4-tetracyanocyclobutane (**21*a***)*

Viscous oil, ^{1}H NMR ($CDCl_3$) δ: 7.87 (d, 1H, J=4 Hz), 7.60 (d, 1H, J=5 Hz), 7.24 (dd, 1H, J_1=5 Hz, J_2=4 Hz), 4.80 ppm (s, 1H); MS, *m/z* (relative abundance): 352 (0.5%), 192 (5), 176 (100). Elemental analysis: found: C 61.30, H 4.51, N 15.97, S, 18.12. Calc. for $C_{18}H_{16}N_4S_2$: C 61.34, H 4.58, N 15.90, S 18.19%.

2.20. *r-1,t-2-Di-(2-furyl)-3,3,4,4-tetracyanocyclobutane (**21*b***)*

Viscous oil, ^{1}H NMR ($CDCl_3$) δ: 7.68 (m, 1H), 6.97 (m, 1H), 6.58 (m, 1H), 5.10 ppm (s, 1H); MS, *m/z* (relative abundance): 320 (1%), 160 (100). Elemental analysis: found C 67.54, H, 5.09, N 17.43. Calc. for $C_{18}H_{16}N_4O_2$: C 67.49, H 5.03, N 17.49%.

2.21. *Quantum yields*

The quantum yield of the photochemical conversion of **10a** was determined using phenylglyoxylic acid as actinometer [14]. A 0.1 M solution of phenylglyoxylic acid in CH_3CN–H_2O (3.1) (10 ml) was irradiated for 600 s under nitrogen in a quartz tube which was surrounded by a quartz water-jacket connected to a Haake F3 thermostat to maintain the temperature at 25.0±0.1°C. A 125 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket was used for irradiation. The mixture was then extracted with CH_2Cl_2 and dried (Na_2SO_4). The removal of the solvent gave a crude product that was dissolved in $CDCl_3$ and analysed by ^{1}H NMR. The chemical conversion was calculated from the integrated ortho protons of the phenyl ring of phenylglyoxylic acid at δ=8.1 and of benzaldehyde at δ=7.9 with reference to the meta and para ring protons at δ=7.6. Φ is assumed to be 0.7. Compound **10a** (300 mg) was dissolved in acetonitrile (10 ml) in a quartz tube which was surrounded with a quartz water-jacket connencted to a Haake F3 thermostat to maintain the temperature at 25.0±0.1°C. The magnetically stirred solution was irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz) which was surrounded by a Pyrex water-jacket. After 1 h, the solvent was evaporated and the mixture was analysed via ^{1}H-NMR.

The intersystem crossing quantum yields were calculated as follows: 0.1 M solution of β-methylstyrene in benzene (10 ml) containing 0.05 M benzophenone was irradiated for 10 min in a Rayonet chamber reactor using medium-pressure 8 W mercury lamps with output centred at 350 nm The mixture was analysed by GLC. In the case of compound **10a** a solution of this compound showing the same optical density (at 360 nm) of that containing the actinometer was used [15].

3. Results and discussion

The photochemical irradiation of 1,3-dithienyl-2-propen-1-one (**10a**) in acetonitrile for 24 h gave a mixture of four products (Scheme 2). It is noteworthy that in a previous paper the photochemical dimerisation of **10a** was described to occur only in 4% overall yield [16]. In our experiment we obtained the dimers in 62% yield (Table 1).

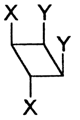
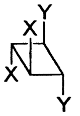
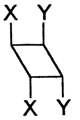
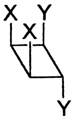
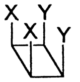
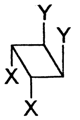
If the reaction was carried out in the presence of benzophenone as triplet sensitiser, no significant modification of the photochemical behaviour of **10a** was observed. Furthermore, the reaction is not quenched in the presence of oxygen. The intersystem crossing quantum yield (Φ_{isc}) of **10a** was 0.04 while the quantum yield of the reaction (Φ) was 0.1. All these data are in agreement with a mechanism involving the first excited singlet state. This hypothesis was tested by using PM3-RHF semiempirical method: the energy of both the HOMO and the LUMO of the S_0 of **10a** is −9.42 and −1.23 eV, respectively. Furthermore, the energy of the LSOMO and the HSOMO of the excited singlet state of **10a** is −8.00 and −4.17 eV, respectively. The best interaction between the above reported frontier orbitals could be obtained between the LSOMO-S_1 and the HOMO-S_0. However, the LSOMO of the first excited singlet state is not a p orbital and it can not participate to frontier orbital control. The interaction between the HSOMO-S_1 and the LUMO-S_0 (Fig. 1) is in agreement with the formation of head-to-head dimers.

The products obtained in the reaction of **10a** can be rationalised by using the hypothesis that the reaction leads to the formation of the more stable isomers (Table 2).

When the reaction was carried out on the furan derivative **10b** we obtained a mixture of two products **11b** and **13b** with 38% overall yields (Scheme 2, Table 1). The photochemical behaviour of **10b** did not change if the irradiation was performed in the presence of benzophenone. We assumed, then, that, also in this case, the reaction involves the photochemical behaviour of the first excited singlet state. The energy of both the HOMO and the LUMO of the S_0 of **10b** is −9.11 and −0.93 eV, respectively. The energy of LSOMO of S_1 is −7.88 eV, while that of HSOMO is −4.07 eV. Also in this case, the best interaction would be between the LSOMO of S_1 and the HOMO of S_0; however, the LSOMO is not a p orbital. The atomic coefficients of the HSOMO-S_1 and LUMO-S_0 are depicted in Fig. 2. These data are in agreement with the formation of head-to-head dimers.

The heat of formation of the all the possible head-to-head dimers accounts for the formation of the obtained products (Table 2).

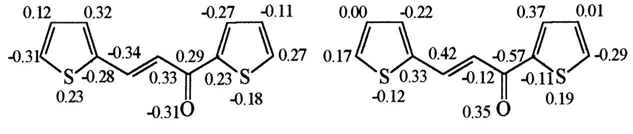
Table 2
Heat of formation of dimers from **10a–d**

Dimer[a]	ΔH_f (kcal mol^{-1})			
	From **10a**	From **10b**	From **10c**	From **10d**
	89	−56	17	15
	82	−63	9	11
	89	−57	22	15
	93	−55	22	17
	107	−46	35	27
	89	−56	16	16

[a] For dimers obtained from **10a**: X: 2-thienyl, Y: CO-(2-thienyl); for dimers obtained from **10ab**: X: 2-furyl, Y: CO-(2-furyl); for dimers obtained from **10c**: X: 2-thienyl, Y: CO-(2-furyl); for dimers obtained from **10d**: X: 2-furyl, Y: CO-(2-thienyl).

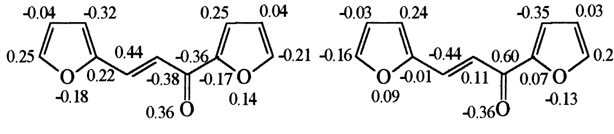
We carried out the photochemical dimerisation also with compounds **10c** and **10d**, which show both a thienyl and a furyl ring in the same molecule. The irradiation, without sensitiser, of **10c** led to the formation of **11c** and **14b** with an overall yield of 57% (Scheme 2, Table 1). Furthermore, the irradiation of compound **10d** led to the formation of a mixture of three products (**11d**, **12b**, and **13c**) with an overall yields of 79% (Scheme 2, Table 1). Also in this case the reaction seems to involve the first excited singlet state.

In the case of **10c**, the energy of the HOMO in the ground state is −9.34 eV, while the LUMO shows an energy of −1.15 eV; the first excited singlet state of **10c** shows the LSOMO at −6.89 eV and the HSOMO at −3.75 eV. The best interaction could be obtained between HOMO-S_0 and LSOMO-S_1. These frontier orbitals are represented in Fig. 3 and they show that only the formation of head-to-head



LUMO-S_0 HSOMO-S_1

Fig. 1. Frontier orbitals of **10a**.



LUMO-S_0 HSOMO-S_1

Fig. 2. Frontier orbitals of **10b**.

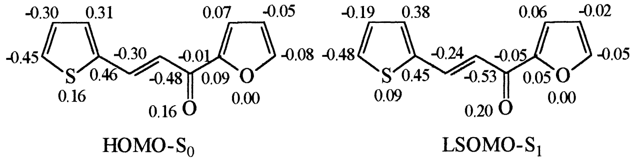


Fig. 3. Frontier orbitals of **10c**.

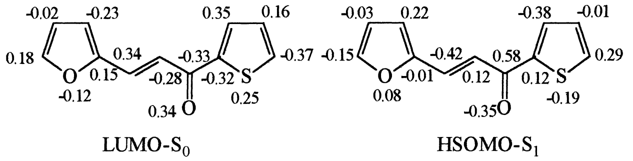


Fig. 4. Frontier orbitals of **10d**.

dimers is allowed. In the case of **10d** the energy of the HOMO-S_0 is −9.11 eV, while that of the LUMO is −1.11 eV; in the first excited singlet state the LSOMO and the HSOMO show the energy of −7.96 and −4.14 eV, respectively. The best interaction in this case would be that between the LSOMO-S_1 and the HOMO-S_0: however, the LSOMO is not a π orbital. The atomic coefficients of both the HSOMO-S_1 and the LUMO-S_0 are represented in Fig. 4, showing that, also in this case, only head-to-head dimers are allowed.

The analysis of the heat of formation of all possible head-to-head dimers are in agreement with the hypothesis that only the more stable isomers are obtained (Table 2).

We tested also the photochemical reactivity of 2-(2-heteroaryl)-nitroethene derivatives. These compounds were irradiated in acetonitrile in the presence of benzophenone as triplet sensitiser. The results are summarised in Scheme 3 and Table 3.

The irradiation of the thienyl derivative **15a** did not give the formation of the expected dimers but gave a mixture of three products where **16a** was the main product. These compounds are dimers of the substrate with the loss of HNO_2. The same behaviour was observed in the case of the furan derivative **16a**. In this case, we observe the formation of two products where **16b** is analogue to that obtained with **15a** and a cyclobutene derivative **19a**, probably deriving from a photochemical reaction on a dimer of the type **16–18**.

The HOMO of the ground singlet state of **15a** is shown in Fig. 5 and it was at −10.09 eV. The LUMO of the S_0 state was at −1.75 eV (Fig. 5). The LSOMO of the lowest excited triplet state was at −6.58 eV while the HSOMO was at −3.00 eV (Fig. 6). The best interaction between the frontier orbitals can be obtained between HSOMO-T_1 and LUMO-S_0. We can note the total superposition of the frontier orbital involved.

Table 3
Photochemical reactions of compounds **15**

Substrate	Irradiation time (h)	Product	Yield (%)
15a	72	**16a**	35
		17a	5
		18a	2
15b	72	**16b**	5
		19a	5

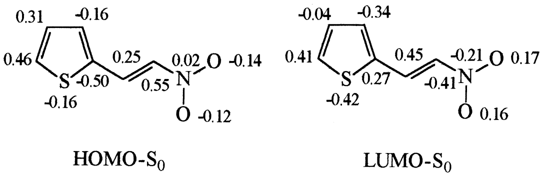


Fig. 5. Frontier orbitals of S_0 state of **15a**.

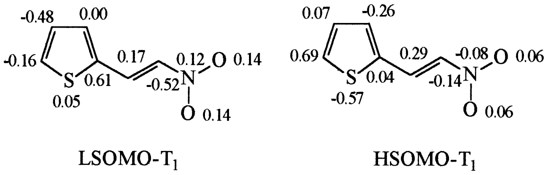


Fig. 6. Frontier orbitals of T_1 state of **15a**.

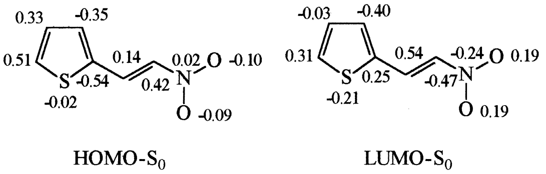


Fig. 7. Frontier orbitals of S_0 state of **15b**.

The HOMO of the ground state of **15b** was at −9.78 eV and the LUMO was at −1.52 eV (Fig. 7). The LSOMO and the HSOMO the lowest excited triplet state of the same molecule was at −6.94 and −4.54 eV, respectively (Fig. 8). The best interaction can be obtained between the HOMO-S_0 and the LSOMO-T_1. We can see that these frontier orbitals can not superimpose.

The data can explain the observed behaviour of **15a** and **15b**. When the superposition of the frontier orbitals allowed the reaction, as in the case of **15a**, we obtained reasonable yields of the products. We do not obtain cyclobutanes, but probably this behaviour depends on the fate of the biradical intermediate deriving from the coupling between the

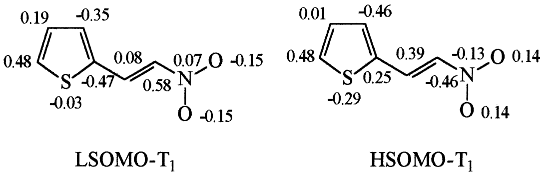
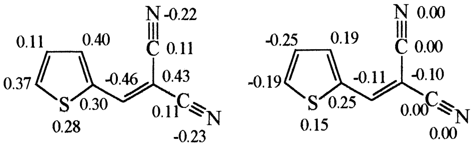


Fig. 8. Frontier orbitals of T_1 state of **15b**.

Table 4
Photochemical dimerisation of compounds **20**

Substrate	Sensitiser	Irradiation time (h)	Product	Yields (%)
20a	Ph_2CO	72	**21a**	3.4
20b	$PhCOCH_3$	72	**21b**	1.5



LUMO S_0 **HSOMO T_1**

Fig. 9. Frontier orbitals of **20a**.

triplet state of the substrate and the ground state of the same molecule. In the case of the furan derivative **15b**, the reaction is not frontier orbitals allowed and we observed only very low yields of the products.

Finally, we tested the sensitised photochemical dimerisation of 1,1-dicyano derivatives **20a-b** (Scheme 4). The irradiation of **20a** in the presence of benzophenone gave the dimer **21a** in 3.4% yield (Table 4). The compound **20b** did not react in the presence of benzophenone, while, when acetophenone was used as sensitiser, the formation of a dimer was observed in very low yield (Table 4).

The HOMO of **20a** was at -9.79 eV while the LUMO was at -1.82 eV. The triplet state of **20a** showed the LSOMO at -6.40 eV and the HSOMO at -2.87 eV. The best interaction can be obtained between the LUMO-S_0 and the HSOMO-T_1: these frontier orbitals are depicted in Fig. 9.

In conclusion, we have seen that heterocyclic substituted propenones can dimerise with good efficiency when irradiated without a sensitiser. Furthermore, we have shown that nitro substituted heterocyclic alkenes can give dimeric products, but that they are not able to give cyclobutanes. Finally, 1,1-dicyano derivatives gave the dimers in very low yields. The present study confirms that the frontier orbital approach can be used in order to describe the dimerisation reaction of this type of compounds. Furthermore, the analysis of the dimers confirms that only the more stable ones can be obtained in the photochemical reactions.

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