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# $\gamma$ -Methylene chalcogenapyrans and benzopyrans as proaromatic donors in “push–pull” Fischer type carbene complexes: Influences of chalcogen atom and chain length on the electronic and N.L.O. properties of these molecules

N. Faux <sup>a</sup>, B. Caro <sup>a,\*</sup>, F. Robin-Le Guen <sup>a</sup>, P. Le Poul <sup>b</sup>, K. Nakatani <sup>c</sup>, E. Ishow <sup>c</sup>

<sup>a</sup> *Laboratoire de chimie organometallique et hétérocyclique, U.M.R. CNRS 6509, Organométalliques et catalyse, Institut de Chimie de Rennes, I.U.T. Lannion, rue E. Branly, 22300 Lannion, France*

<sup>b</sup> *U.C.O. 22200 Guingamp, France*

<sup>c</sup> *Laboratoire de Photophysique et de Photochimie Supra et Macromoléculaires, UMR 8531, Ecole Normale Supérieure de Cachan, 61 avenue du président Wilson, 94235 Cachan cédex, France*

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## Abstract

A new class of push–pull molecules bearing  $\gamma$ -methylene chalcogenapyran and benzopyran nucleus as proaromatic donors and methoxypentacarbonyltungstene carbene fragment as acceptors is described. N.L.O. properties (as  $\mu\beta$  by EFISH) of these complexes have been investigated. The influence of the unsaturated chain length, of the presence of the fused aromatic ring and of the chalcogen atom on the first hyperpolarizability values are shown.

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## 1. Introduction

Due to the potential applications in the field of optoelectronics during the last two decades, intense research has been conducted to discover organic or organometallic molecular materials with non-linear optical properties [1]. From a simple theoretical model developed by Chemla and Oudar [2] about thirty years ago, based on a sole electronic transition (the two-level model), organic and organometallic compounds with large first hyperpolarizability  $\beta$  have been synthesized. In the approximation of the two-level model,  $\beta$  is directly pro-

portional to  $\Delta\mu_{eg}$ , the difference between the excited and the ground state dipole moment, to  $f_{eg}$  the transition dipole moment, and inversely proportional to the energy of the electronic transition  $\Delta E_{ge}$  implied in the N.L.O. phenomena ( $\beta\alpha(3f_{eg}^2\Delta\mu_{eg}^2)/(\Delta E_{ge}^3)$ ).

Purely organic push–pull molecules in which donor and acceptor groups are linked via unsaturated  $\pi$  spacers (Fig. 1) fit the model since they are characterized, particularly for extended spacers, by a low energy intramolecular charge transfer electronic transition  $\Delta E_{ge}$ , a large transition dipole moment  $f_{eg}$ , and a significant  $\Delta\mu_{eg}$  [3].

The two-level model has been applied, but with some limitations, to organometallic push–pull molecules which possess a low energy metal to ligand electronic charge transfer transition [4]. For example, in ferrocenyl push–pull molecules, the presence of two electronic

\* Corresponding author. Tel.: +33 2 96485748; fax: +33 2 96485797.  
E-mail addresses: bertrand.caro@iut-lannion.fr (B. Caro), francoise.le-guen@univ-rennes1.fr (F. Robin-Le Guen).

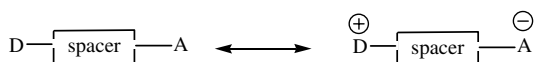


Fig. 1. Schematic representation of push-pull chromophore.

transitions in the visible spectrum, which play a role in the N.L.O. phenomena does not allow a simple analysis based on this model [5].

Semi-empirical calculations [6] and experimental work [3c] have shown that  $\beta$  can be correlated with the ground state polarization. In a simple description of donor-acceptor molecules as a mixture of neutral and zwitterionic limit resonance forms (Fig. 1),  $\beta$  values peak positively when there is at least 75% of the neutral form present, decreases to zero when both forms have been equally (the so-called cyanine limit) present and becomes negative when the zwitterionic form prevails. It has been emphasized that the  $\beta$  evolution closely follows that of  $\Delta\mu_{eg}$  [6a].

For a given molecular structure, several factors can influence the balance between the two limit resonance forms. For example, increasing the donor or acceptor strength of the end groups tends to increase the weight of the zwitterionic form. Increasing the length of the  $\pi$ -spacer favours the neutral form. Aromaticity and proaromaticity of the end capped groups can also play a major role by stabilizing, respectively, the neutral and the zwitterionic limit forms. Among the used acceptor groups, heterocyclic proaromatic substituents (barbituric group for example [3c]) have shown their efficiency, particularly in molecule containing aromatic donor groups. In these cases, the decrease of resonance energy upon charge transfer was offset by the gain of aromaticity at the other end of the molecule.

On the other hand, the influence of proaromatic heterocyclic donors on N.L.O. properties of this class of molecules have been less studied. Studies focused on N.L.O.-phores containing five atom proaromatic heterocycles (dithiafulvene for example [7]).

$\gamma$ -Methylene chalcogenapyran and benzochalcogenapyran nucleus and chalcogenaxanthene act as versatile six atom nucleus in heterocyclic chemistry (Fig. 2). We can find them in many compounds with potential applications in the field of conductive [8], magnetic [9] and

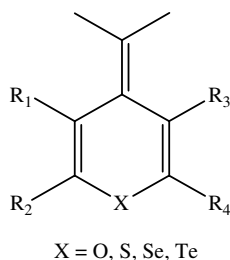


Fig. 2. Methyleneprane core.

liquid crystals materials [10], in photodynamic therapy [11] and in molecular machines [12].

In addition,  $\gamma$ -methylene pyran structure bearing two cyano groups has been tested as proaromatic acceptors for N.L.O. purposes [13]. We anticipate that this heterocyclic fragment could also act as a proaromatic donor in push-pull type molecules.

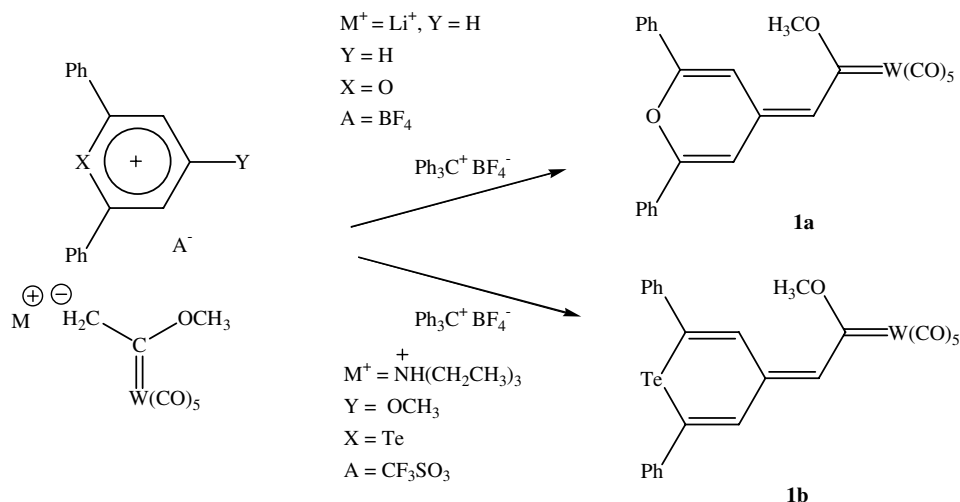
In this paper, we wish to report on the synthesis and N.L.O. properties of  $\gamma$ -methylene chalcogenapyran and benzochalcogenapyran Fischer type methoxy carbene complexes. In these molecules, a strong electron withdrawing organometallic acceptor fragment is linked via an unsaturated carbon-carbon chain of various lengths to the heterocycle. It can be noted that methoxy and amino Fischer carbene complexes containing classic dimethyl amino and ferrocenyl donor groups have given large first hyperpolarisability  $\beta$  values determined by the HRS technique and the results have been analysed in the context of the two-level model [14] despite the presence of more than one transition in the visible part of the electronic spectrum. In fact, the role of the organometallic carbene fragment is not well understood. For amino carbene complexes, polarisation of  $\pi$  cloud of the unsaturated link by the electronic inductive effect of the metal carbonyl would be responsible for the important N.L.O. response. The role of the MLCT (metal to ligand charge transfer) is minimized due to the lack of conjugation between the unsaturated chain and the carbenic fragment.

For this study, we focussed on the influences of chalcogen (O, S, and Te) and the unsaturated chain length, both on the electronic ground state structure and on the second order non linear optical properties. As the group 6 atom becomes more and more electropositive (O < S < Te), the conjugation with the acceptor group should increase. However, this favourable effect is offset by a less efficient overlap of the lone pair orbitals of the heteroatom with those of the  $\pi$  framework [15]. The existence of two opposite electronic effects, which also determines the aromaticity of the heterocycle [16], does not allow, "a priori" an estimate of the second order non-linear optical properties.

## 2. Results and discussion

### 2.1. Synthesis

We have previously described the synthetic methodology which has allowed the formation of the complexes necessary for this study. The first molecule of the series **1a** (Scheme 1) was obtained from unsubstituted  $\gamma$ -pyrylium salts and Fischer carbene complexes [17]. The use of the  $\gamma$ -methoxytelluropyrylium salt (Y = OMe, Scheme 1), allowed the formation of the carbene **1b** in good yield. This synthetic approach should open the route to a great



Scheme 1.

variety of heterocyclic carbene complexes and will be the subject of a future communication [18].

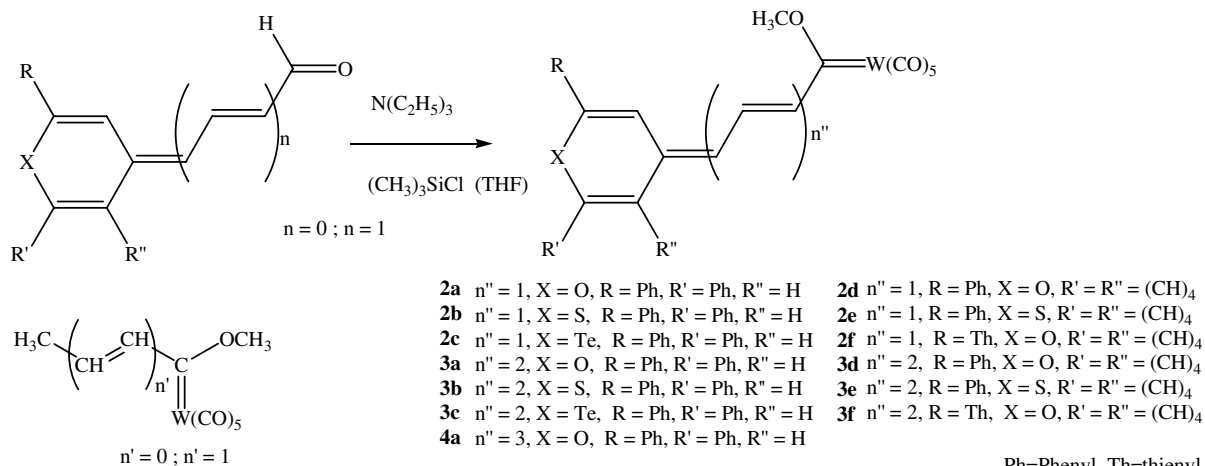
The type **2** molecules were obtained from Aumann condensation [19] using heterocyclic aldehydes  $n = 0$  (Scheme 2) and the carbanion of the corresponding carbene, in the presence of  $N(Et)_3$  and  $(CH_3)_3SiCl$  (Scheme 2) [20]. Action of the propenyl carbene complex (Scheme 2,  $n' = 1$ ), under the same conditions, on the aldehyde  $n = 0$  (Scheme 2), gave the unsaturated carbene **3** with good to moderate yield [20]. The most extended molecule **4a** was obtained in low yield from the heterocyclic aldehyde  $n = 1$  (Scheme 2) and the propenyl Fischer type carbene complex ( $n' = 1$ ).

All the new compounds were characterized by FT-IR, NMR ( $^{13}C$  and  $^1H$ ), UV-Vis spectroscopy and elementary analysis or mass spectroscopy (**2b**, **2c**, **3b**, **3c**, **4a**, **2d-f**, **3d-f**). For the highly unsaturated complexes, the  $^3J_{HH}$  coupling constant values are consistent (see experimental part) with a trans configuration for the C–C

double bonds. We have reported, respectively, in Tables 1 and 2 a summary of the linear optical data obtained for chalcogenapyran and benzochalcogenapyran carbene complexes in two solvents of different polarity.

The second order non linear properties were studied in  $CHCl_3$  solution at  $1.97 \mu m$  by an electrical field induced second harmonic generation technique, which provides information about the scalar product  $\mu\beta$  ( $2\omega$ ) of the vectorial part of the first hyperpolarisability tensor and the dipole moment vector  $\mu$ .

All complexes were thus tested away from resonance. These values are reported in Table 3 together with the  $\Delta J$  calculated from  $^3J_{HH}$  coupling constants relating to the hydrogen atoms of the unsaturated chain. It is well established that these values provide information about the degree of bond length alternation of unsaturated carbon–carbon chains [3c]. Therefore, the reported  $\Delta J$  values could be indicative of the pyrylium character of the heterocycles.



Scheme 2.

Table 1

Absorption data of  $\gamma$ -methylenechalcogenapyran carbene complexes in  $\text{CCl}_4$  and DMSO (Schemes 1 and 2),  $\lambda$  (nm)  $\epsilon$  ( $\times 10^{-4} \text{ mol}^{-1} \text{ L cm}^{-1}$ )

	$\text{CCl}_4$		DMSO	
	$\lambda 1$ ( $\epsilon$ )	$\lambda 2$ ( $\epsilon$ )	$\lambda 1$ ( $\epsilon$ )	$\lambda 2$ ( $\epsilon$ )
<b>1a</b>	334 (1.2)	542 (2.3)	356 (0.87)	515 (1.8)
<b>1b</b>	442 (0.9)	583 (3.4)	440 (1.3)( $\text{CH}_3\text{CN}$ ) <sup>b</sup>	573 (1.7)( $\text{CH}_3\text{CN}$ ) 590 <sup>c</sup>
<b>2a</b>	449 (0.35)	569 (1.1)	454 (0.61)	590 (2.7)
<b>2b</b>	468 (1.2)	585 (4.5)	464 (1.1)	612 (4.2)
<b>2c</b>		598 (5.7) <sup>a</sup>		628 (2.6) <sup>a</sup>
<b>3a</b>		594 (7.6) <sup>a</sup>		653 (2.3) <sup>a</sup>
<b>3b</b>		605 (7.3) <sup>a</sup>		652 (2.4) <sup>a</sup>
<b>3c</b>		613 (5.7) <sup>a</sup>		639 (3.2) <sup>a</sup>
<b>4a</b>		619 (2.3) <sup>a</sup>		665 (2.4) <sup>a</sup>

<sup>a</sup> A sole band is observable for the two electronic transitions.<sup>b</sup> In DMSO, an oxidation leads to the production of an ester.<sup>c</sup>  $\epsilon$  undetermined.

Table 2

Absorption data of methylenebenzochalcogenapyran carbene complexes in  $\text{CCl}_4$  and DMSO (Scheme 2),  $\lambda$  (nm)  $\epsilon$  ( $\times 10^{-4} \text{ mol}^{-1} \text{ L cm}^{-1}$ )

	$\text{CCl}_4$		DMSO	
	$\lambda 1$ ( $\epsilon$ )	$\lambda 2$ ( $\epsilon$ )	$\lambda 1$ ( $\epsilon$ )	$\lambda 2$ ( $\epsilon$ )
<b>2d</b>	450 (1.2)	558 (3.6)	446 (0.8)	575 (2.6)
<b>2e</b>		571 (3.6) <sup>a</sup>		582 (1.8) <sup>a</sup>
<b>2f</b>	463 (1.2)	565 (3.6)	450 (0.9)	580 (2.6)
<b>3d</b>		576 (2.6) <sup>a</sup>		599 (2.0) <sup>a</sup>
<b>3e</b>		583 (2.0) <sup>a</sup>		601 (1.6) <sup>a</sup>
<b>3f</b>		579 (2.3) <sup>a</sup>		607 (1.5) <sup>a</sup>

<sup>a</sup> A sole band is observable for the two electronic transitions.

Table 3

 $\mu\beta$  and  $\overline{\Delta J}$  values for complexes 1–4

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>4a</b>	<b>2d</b>	<b>2e</b>	<b>2f</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>
$\mu\beta^b \times 10^{-48} \text{ esu}$	−51	19	505	665	673	1219	2348	1615	2894	219	402	505	1027	870	937
$\overline{\Delta J}$ (Hz) (THF- $d_8$ )			0.4	0.7	1.1 <sup>a</sup>	1.2	1.9	1.4 <sup>a</sup>	2.2 <sup>a</sup>	1.8	0.6	1.3	2.0	1.9	2.4

 $\overline{\Delta J}$  values average difference in  $^3J_{\text{HH}}$  values ( $^1\text{H}$ – $^1\text{H}$  coupling constants) across adjacent C=C and C–C bonds.<sup>a</sup> Measurements in  $\text{CDCl}_3$ .<sup>b</sup> Molecular concentrations used for the measurements were in range  $10^{-3}$ – $10^{-2}$  M; 3-methyl-4-nitrosaniline (MNA) for which  $\mu\beta$  ( $\text{CHCl}_3$ ) =  $71.06 \times 10^{-48} \text{ esu}$  was used as an external reference.  $\mu\beta \pm 20\%$ .

## 2.2. Electronic transitions and N.L.O. properties

The first compounds of the series examined in this study (**1a**, **1b**) have shown two strong absorption bands in the UV–Vis, which exhibit solvatochromic behaviour (Table 1). The corresponding electronic transitions should play a role in the first quadratic hyperpolarisability. On the base of DFT calculations performed on the model of **1a** [17], the lower and the higher energy bands can be assigned, respectively, to a metal to ligand charge transfer transition (MLCT or HOMO–LUMO) and to a  $\pi$ – $\pi^*$  intra ligand charge transfer transition (ILCT). The electronic spectra show a third band in the UV (not shown in Table 1). This band, insensitive to solvent polarity, can be tentatively assigned to a  $d$ – $\pi^*\text{CO}$  transition. As observed earlier for other “push–pull” molecules, increasing conjugation length leads to a red shift of the

solvatochromic bands (Tables 1 and 2) [3,14]. However, the  $\pi$ – $\pi^*$  transition (ILCT) seems to be more sensitive to this factor. This result leads, for compounds **3–4**, to the observation of an overlap of the ILCT and MLCT bands. As a consequence, for two transitions it was not possible to obtain values of the oscillator strength ( $f_{\text{eg}}$ ).

Under the influence of the heteroatomic substitution (O–S–Te), a bathochromic shift was observed. Such behaviour has been previously noted by Dettý for pyrylium and chalcogenapyrylium salts [15]. For these cations a concomitant lowering and increase, respectively, of  $\pi$  and  $\pi^*$  (HOMO, LUMO) levels as the size of the heteroatom raises, is responsible for the red shift. Substitution of a phenyl group by a thiophenyl group (compounds **2f**, **3f**) leads to a red shift for the ILCT (when it is observable) and for the MLCT (Table 2). Finally, it can be noted that the high MLCT wavenumber values

are consistent with a conjugation between the carbenic  $C(OMe)W(CO)_5$  fragment and the unsaturated part of the molecule, a situation which is different to that found for push–pull amino carbenes [14a].

The  $\mu\beta$  values are presented in Table 3. Since multiple states seem to contribute to the non-linear response, no attempt has been made to correct the values for dispersion using the two-level model.

Apart from compounds **1** which gave low negative (**1a**) or positive (**1b**) values, the observed  $\mu\beta$  values for complexes **2–4** are large and positive indicative of excited states, which are more polarized than the ground state ( $\mu_e > \mu_g$ ). In addition, this implies that the ground and excited states are polarized in the same direction. The positive values are in accordance with the solvatochromism observed for the lower MLCT energy band (Tables 1 and 2). However, if we assume a mainly *s-trans* conformation for the carbene complexes, then this result does not concord with the “direction” of metal to ligand charge transfer which is, as suggested by the valence bond description [14a], opposite to that of the ground state dipole moment. Calculations have shown that ground state dipole moment direction is governed by the pyrylium character of these molecules [21] (Scheme 2). It can be noticed that the  $\overline{\Delta J}$  values ranged from 2.4 to 0 Hz depending on the polyenic chain length, are indicative of reduced bond length alternation and therefore of a pyrylium character [14c] (see Fig. 3).

On the other hand, the negative  $\mu\beta$  value found for **1a**, which is in line with the negative solvatochromism observable for the MLCT band, reflects an opposite sign for  $\mu_e$  and  $\mu_g$  values, or a  $\mu_g$  value greater than that of  $\mu_e$ . For the telluro complex **1b**, the low positive  $\mu\beta$  product, should be relevant to the low solvent influence on the UV–Vis electronic spectrum (Table 1).

Despite the apparent failure of the two-level model (calculations will have to be carried out to explain this behaviour [21]), as it can be noted from Table 3, structural changes affect the N.L.O. response.

As expected from other N.L.O. studies, lengthening the polyenic chain induces a significant increase in the first quadratic non-linearity [3,14]. The enhancement of the first hyperpolarizability is found in the two series (benzo and pyran series). This leads to large  $\mu\beta$  values, particularly for the longest complex **4a** reported here ( $\mu\beta 2894 \times 10^{-48}$  esu).

Appending a benzene ring to the pyran nucleus produces a decrease in the quadratic hyperpolarizability, for homologous “push–pull” carbene complexes of similar length. This is in accordance with the higher energy of the electronic transitions (MLCT and ILCT) corresponding to the chalcogenabenzopyran derivatives (Tables 1 and 2). From a comparison of the values (Table 3), it appears that the ground state of the chalcogenapyran chromophores seems to have a more pronounced chalcogenapyrylium character. Therefore, the pyran nucleus is a better electron donating group than the benzopyran group. Moreover, the presence of a benzene ring (benzopyran derivatives) should partly inhibit the  $\pi$  electron mobility upon photoexcitation influence and as expected, a lower  $\mu\beta$  value is observed.

It is noteworthy that an opposite trend has been found for analogous phenylthiocarbene complexes for which, in particular for the pyran series, the contribution of the zwitterionic form is more pronounced (a more important pyrylium character) [14c].

Replacing the oxygen atom of the pyrylium ring with a sulfur atom enhances the N.L.O. response for all compounds of the heterocycle series, except for **3d** and **3e** for which a slight decrease in the  $\mu\beta$  product is observed. Thus, the thiopyran complex **3b** exhibits a  $\mu\beta$  value of  $2348 \times 10^{-48}$  esu, about twice high as that of the homologous pyran complex **3a**.

In the pyran series, the increase of the  $\mu\beta$  products should be relevant to the greater polarizability of the sulfur valence shell electrons, and to a certain extent to a decrease of heterocyclic aromatic character relative to that of the oxygenate derivatives [15]. This is in a line with the  $\overline{\Delta J}$  values reported in Table 3 for **2a–2b** and **3a–3b**. The relative sensitivity of the N.L.O. response toward the O to S atom change, is not in accordance with the result of a recent theoretical analysis which showed that styrene based chromophores bearing pyrylium and thiopyrylium ring, gave similar  $\mu\beta$  values [23]. In the benzopyran series, the presence of an aromatic benzene ring affects the polarization and the polarizability of the  $\pi$  electrons and the evolution of the first hyperpolarizability, upon O–S substitution could reflect subtle differences in the  $\pi$  electronic transmission capability. Note that in these cases, the effect of the substitution on the  $\mu\beta$  values is sensitive

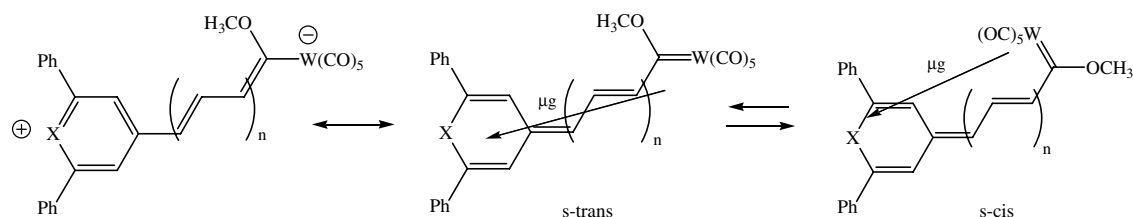


Fig. 3. Orientation of the dipole moment for *s-cis* and *s-trans*.



to the length of the unsaturated chain (Table 3: compared **2d–2e** values and **3d–3e** values).

On the other hand, the telluropyran complexes showed  $\mu\beta$  values close to those of their thio counterparts for compounds of type **2** and lower values for molecules of type **3**. It is well established that the aromaticity of telluropyrylium is weak. In addition, X-ray structure of a telluromethylenepyran pyrylium salt has shown the great distance between the  $C_\alpha$  and Te atoms and the significant distortion of the telluroheterocyclic ring [15]. The tellure atom is bent  $8.7^\circ$  out of the plane formed by the five carbon atoms of the ring. Therefore, the N.L.O. results could be the consequence of a poor overlap between the lone pair electrons of the tellure atom and the  $\pi$  cloud.

Finally, note that substitution of phenyl by thiophenyl group in  $\alpha$  position of the heterocycle doubles the N.L.O. response for shorter complexes (**2d** and **2f**) but has no influence on the carbenes of type **3** (**3d** and **3f**).

### 3. Conclusion

To summarize, we have shown the efficiency of chalcogen and benzochalcogenapyran ring as proaromatic donors in push–pull carbene complexes for N.L.O. purposes. The compounds containing pyran heterocycle, gave a better non-linear response than those bearing a benzopyran ring. The lower values of  $\mu\beta$  for the fused ring compounds should be the consequence of the presence of the benzene ring which limits the  $\pi$  electron circulation. Among the tested proaromatic chalcogenapyran heterocycles (O, S, Te) tested, the thiopyran ring gave the largest  $\mu\beta$  values. This result can be explained by the sulphur atom electronegativity and the polarizability of lone pair electrons, which allow good transmission of the electrons upon photoexcitation.

Calculations are in progress to obtain more information concerning the electronic transitions implied in the N.L.O. phenomena.

### 4. Experimental section

#### 4.1. Materials

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from Na/benzophenone under  $N_2$ . Chromatographic purification was performed with Silica Gel 60 (0.063–0.200  $\mu$ m). NMR analysis was done using Brücker 500 MHz spectrometer. IR analysis were recorded on Perkin–Elmer Spectrum 1000 FT-IR spectrophotometer using KBr plates and elementary analysis or mass spectroscopy were performed by the Centre Régional de Mesures Physiques de l'Ouest de l'Université de Rennes.

#### 4.2. General procedure for preparation of carbenes **2b**, **2c**, **3b**, **3c**, **4a**, **2d**, **2e**, **2f**, **3d**, **3e**, **3f**

In a 100-ml schlenk,  $1.3 \times 10^{-3}$  mol of the corresponding heterocyclic aldehyde was added to 20 ml of freshly distilled THF, under a stream of nitrogen.  $N(Et)_3$  ( $3.9 \times 10^{-3}$  mol),  $(CH_3)_3SiCl$  ( $3.9 \times 10^{-3}$  mol) and the corresponding methoxy carbene ( $1.3 \times 10^{-3}$  mol) were then added successively to the stirred solution at room temperature. The de-gassed reaction mixture was monitored with TLC chromatography. The solution was quenched with iced and de-gassed water under a stream of nitrogen. The complex was then extracted with de-gassed diethylether ( $3 \times 100$  ml) and dried with  $MgSO_4$ . Solvents were removed under vacuum. The obtained residue was then purified on layer chromatography and the complex was then isolated (blue to purple solids). Yields: **2b**, 90%; **2c**, 69%; **3b**, 52%; **3c**, 31%; **4a**, 20%; **2d**, 65%; **2e**, 48%; **2f**, 64%; **3d**, 27%; **3e**, 24%; **3f**, 31%.

#### 4.3. Selected data for **2b**

$^1H$  NMR (THF- $d_8$ , 500 MHz):  $\delta$  4.39 (s, 3H), 6.15 (d,  $J = 12.9$  Hz, 1H), 7.15 (d,  $J = 13.6$  Hz, 1H), 7.19 (s, 1H), 7.45 (m, 6H), 7.61 (s, 1H), 7.67 (m, 4H), 7.94 (t,  $J = 13.2$  Hz, 1H).  $^{13}C$  NMR (THF- $d_8$ , 500 MHz):  $\delta$  67.4, 120.6, 122.7, 127.0, 127.4, 127.5, 130.1, 131.0, 131.1, 137.8, 138.2, 139.0, 141.7, 143.7, 145.1, 148.0, 199.6, 204.7, 292.9. Anal. Calc. for  $C_{27}H_{18}O_6SW$ : C, 49.56; H, 2.77; S, 4.90. Found: C, 49.39; H, 3.17; S, 5.29%. FTIR (KBr): 2922, 2050, 1929, 1885, 1547, 1488, 1143, 1096, 964, 897, 868, 748, 686. M.p. = 138 °C.

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### Appendix A. Supplementary materials

Supporting characteristic data for the new compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.049.

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