Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 49 (2008) 1323–1327
Tetrahedron Letters

Quantification of the push–pull character of the isophorone chromophore as a measure of molecular hyperpolarizability for NLO applications

Erich Kleinpeter[a,*], Andreas Koch[a], Bozhana Mikhova[b], Bistra A. Stamboliyska[b], Tsonko M. Kolev[b]

[a] *Chemisches Institut der Universität Potsdam, Karl-Liebnecht Str. 24-25, D-14476 Golm, Germany*
[b] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, Bonchev Str., Building 9, Sofia 1113, Bulgaria*

Received 6 July 2007; revised 18 December 2007; accepted 19 December 2007
Available online 25 December 2007

Abstract

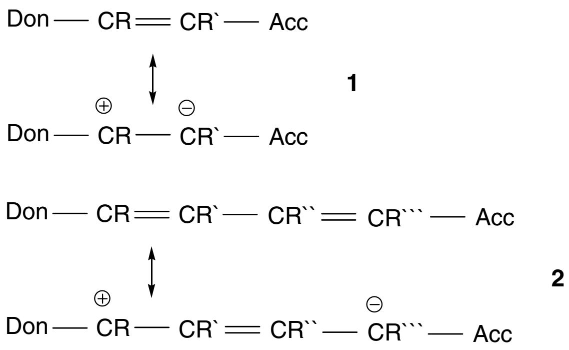
The push–pull character of a series of *para*-phenyl substituted isophorone chromophores has been quantified by the ^{13}C chemical shift difference of the three conjugated partial C=C double bonds and the quotient of the occupations of both the bonding and anti-bonding orbitals of these C=C double bonds as well. The correlations of the two push–pull quantifying parameters, and to the corresponding bond lengths, strongly recommend $\pi^*_{C=C}/\pi_{C=C}$ as the general parameter to estimate *charge alternation* and as a very useful indication of the molecular hyperpolarizabilities for NLO application of the compounds studied.

Keywords: Push–pull character; Push–pull quotient $\pi^*_{C=C}/\pi_{C=C}$; Isophorone chromophore; Molecular hyperpolarizability; NLO application; ^{13}C NMR spectroscopy

1. Introduction

A characteristic feature of push–pull alkenes **1** or extended chromophores, for example, **2** (Scheme 1), is charge alternation concomitant with bond length alternation (BLA). Thus, along with charge alternation, the bond orders of C=C double bonds are increased whilst the orders of any intervening C–C single bonds is reduced, that is, the corresponding bond lengths are shortened and elongated, respectively.[1]

In addition to bond lengths (experimentally available for the solid state by X-ray crystallography), a number of other indicators have been employed to quantify the *push–pull effect*. These include the barrier to rotation, $\Delta G^{\neq}_{c}$, about the partial C=C double bond,[1] the ^{13}C chemical shift difference, $\Delta\delta_{C=C}$, of the carbon atoms of the C=C double bond,[2] and the quotient of the occupations of the bonding (to quantify the acceptor activity) and anti-bonding orbitals (to quantify the donor activities) of the C=C double bonds.[3a]



Scheme 1.

---

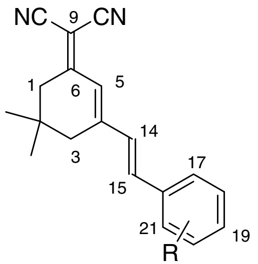
[*] Corresponding author. Tel.: +49 331 977 5210/5211; fax: +49 331 977 5064/5057.
E-mail address: kp@chem.uni-potsdam.de (E. Kleinpeter).

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.12.107

This latter parameter is denoted as $\pi_{C=C}/\pi^*_{C=C}$[3a] or the *push–pull quotient*. However, rotational barriers are accessible[3a] by NMR spectroscopy only when they lie below 95.3 kJ mol^{-1} and above 41.5 kJ mol^{-1}[4] whilst $\Delta\delta_{C=C}$ is limited to identical substitution patterns of the C=C double bond.[3b] When either of these parameters are available though, they are excellent measures of charge alternation.[2,3b] In addition to bond lengths, the *push–pull quotient* has also been shown to be a reliable and general parameter to quantify the *push–pull* effect.[4]

Charge alternation in push–pull alkenes is indelibly associated with unusual properties for the members of this class of compounds. In addition to large molecular dipoles, extremely high hyperpolarizabilities[5–9] and strong intramolecular charge-transfer absorption bands are also present.[10] These properties suggest that push–pull alkenes **1** and the extended chromophores **2** are of great promise as potential materials for nonlinear optical (NLO) devices.[7] Here, the required high first-order molecular hyperpolarizability for second-order processes is dependent on an optimal donor/acceptor combination at the chromophore, in other words, on the *push–pull effect*. More work, though, is required to fully understand the resultant effects of the substituents (their number, positional isomerism, donor–acceptor strength and combination, preferred conformation, and, finally, solution properties)[11] because, for this aspect, only one combination of the substituents at the chromophore is usually effective and the underlying reason for this is not yet understood.

Isophorone chromophores **3** (Scheme 2) are highly promising functional dyes for photonic materials[12] and have been demonstrated to provide efficient photochromic response in materials for holographic-optical data storage[13,14] and in organic photorefractive materials.[15] For example, it has been demonstrated that isophorone/combined isophorone-thiophene chromophores have extremely high electro-optic properties.[15] It is the aim of this Letter to report a number of ionophore chromophores **3** with respect to the push pull character present and the potential NLO applications as well.



3

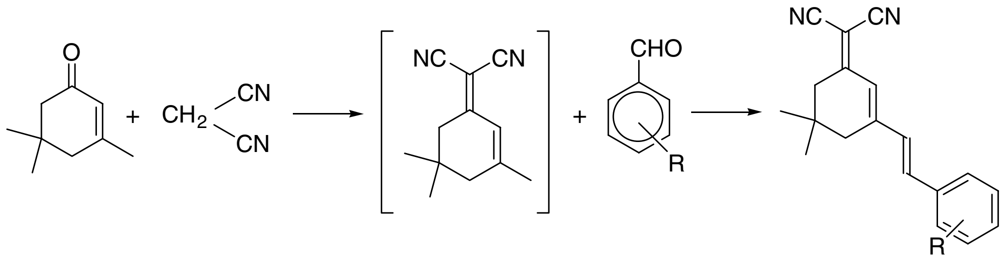
R = H **3a**
R = 2-OMe **3b**
R = 4-OH **3c**
R = 4-OMe **3d**
R = 2.4-OMe **3e**
R = 4-NMe$_2$ **3f**

Scheme 2.

2. Results and discussion

Isophorone chromophores **3a**–**f** were synthesized by a one-pot procedure[16a,b] from isophorone, maleonitrile and the corresponding donor-functionalized benzaldehyde (see Scheme 3). Both the IR spectra[17] and X-ray structures of **3a**–**f** have already been published[12,18] whilst the ^{13}C NMR chemical shifts are now presented in Table 1. It was considered prudent that by varying both the position and donor activity of the phenyl substituent, both the chemical and physical properties of these compounds could be tuned and the structural variations assessed by ^{13}C NMR spectroscopy. Therefore, the ^{13}C chemical shifts were calculated at the density functional theory (DFT) level and compared with the occupation quotient;[4] the results are included in Table 1. At the same level of theory, the molecular hyperpolarizabilities at zero frequency $\beta(0)$ were also calculated to estimate the NLO efficiency of the chromophores studied; these results are presented in Table 2. It can be seen that compounds with stronger donors show higher $\beta(0)$ values than those with weaker donors. The dimethylamino compound **3f**[19] was not only found to have the highest value within the elucidated series, but moreover, it dramatically excels in its β value compared to the 2,4-dimethoxy derivative **3e**.

The bond polarization-indicating parameters, $\Delta\delta_{C=C}$ and $\pi_{C=C}/\pi^*_{C=C}$, calculated at the same level of theory, are collected in Table 3. Both can be correlated to the corresponding bond lengths (see Fig. 1) and are thus proven to be useful. From **3a** to **3f**, charge polarization along the isophorone chromophore increases, and $\Delta\delta_{C=C}$ also significantly increases as well. Despite the donor substituents on the phenyl group being distal, the correlations are nevertheless excellent. In the case of the $C_{14}{=}C_{15}$ double bond,



3a-f

Scheme 3.

Table 1
^{13}C chemical shifts of isophorone chromophores **3**

Compound		^{13}C chemical shifts of carbon atoms																			Subst.	Subst.
		1	2	3	4	5	6	7	8	9	10	12	14	15	16	17	18	19	20	21		
3a	Calc.	45.8	38.2	41.8	160.2	131.2	176.3	25.9	32.7	83.7	116.2	117.2	133.3	143.2	141.2	128.7	133.6	135.5	133.7	137.1		
	Exp.	43	32	39.2	153.8	123.5	169.2	28	28	78.7	112.6	113.4	129.1	137.0	135.6	127.5	129	129.7	129	127.5		
3b	Calc.	45.8	38.2	42.1	161.3	130.2	176.0	25.9	32.6	82.5	116.4	117.3	132.0	136.6	130.2	130.4	125.3	136.7	112.5	165.1	55.5	
	Exp.	43.0	32	39.1	154.8	123.1	169.4	28	28	78	112.8	113.6	129.4	132.1	124.6	127.4	120.9	131	111.1	157.7	55.5	
3c	Calc.	45.8	38.1	41.8	160.3	130.0	175.9	25.9	32.7	82.5	116.4	117.4	130.8	142.2	133.8	131.5	120.8	166.5	115.2	138.5		
	Exp.	43	32	39.2	154.3	122.8	169.4	28	28	77.8	112.9	113.7	127.1	136.7	128.7	129.4	116.1	157.2	116.1	129.4		
3d	Calc.	45.9	38.1	42.0	161.4	128.8	175.8	25.9	32.7	80.9	116.7	117.7	129.3	136.1	122.7	131.8	115.5	170.5	93.0	166.5	55.3	55.2
	Exp.	43.1	32	39.2	155.4	122.3	169.4	28	28	76.9	113.2	113.9	127.2	132.2	117. 9	128.8	105.6	162.5	98.5	159.2	55.6	55.5
3e	Calc.	45.8	38.2	41.8	160.5	129.8	176.0	25.9	32.7	82.2	116.5	117.5	130.7	142.6	133.8	130.6	124.0	169.3	111.9	138.9	55.7	
	Exp.	42.9	31.9	39.1	154.3	122.5	169.2	27.9	27.9	77.5	112.9	113.6	126.8	136.8	128.3	129.1	114.4	161	114.4	129.1	55.3	
3f	Calc.	45.9	38.1	41.9	160.8	128.2	175.4	25.9	32.8	80.2	116.9	117.9	128.2	143.2	129.7	131.0	115.5	155.5	114.1	139.1	41.8	41.9
	Exp.	42.9	31.9	39.2	155.2	121.4	169.1	28	28	75.7	113.4	114.2	124.4	138	129.4	129.4	112.3	151.2	112.3	129.4	40.3	40.3

Table 2
Theoretical calculation (B3LYP/6-311G*) of the molecular hyperpolarizabilities at zero frequency $\beta(0)$ of isophorone chromophores **3**

Compound	R Substituent	$\beta(0)$ (10^{-50} C V^{-2} m^3)
3a	H	17.52
3b	2-OMe	22.76
3c	4-OH	34.66
3d	4-OMe	41.31
3e	2,4-OMe	42.06
3f	4-NMe$_2$	74.92

Table 3
The ^{13}C chemical shift differences, $\Delta\delta_{C=C}$, of the three partial C=C double bonds together with the corresponding *push–pull effect* and the mean *push–pull effect* of isophorone chromophores **3**

		$C_9{=}C_6$		
	π	π^*	π/π^*	$\Delta\delta$(C6–C9)
3a, H	1.7765	0.2788	0.1569	90.5
3b, 2-OMe	1.7752	0.2863	0.1613	91.4
3c, 4-OH	1.7753	0.2872	0.1618	91.6
3d, 4-OMe	1.7751	0.2886	0.1626	91.7
3e, 2,4-OMe	1.7735	0.2970	0.1675	92.5
3f, 4-NMe$_2$	1.7724	0.3030	0.1710	93.4
		$C_4{=}C_5$		
	π	π^*	π/π^*	$\Delta\delta$(C4–C5)
3a, H	1.7479	0.2008	0.1149	30.3
3b, 2-OMe	1.7428	0.2080	0.1193	31.7
3c, 4-OH	1.7445	0.2105	0.1207	31.5
3d, 4-OMe	1.7437	0.2117	0.1214	31.8
3e, 2,4-OMe	1.7380	0.2202	0.1267	33.1
3f, 4-NMe$_2$	1.7361	0.2273	0.1309	33.8
		$C_{14}{=}C_{15}$		
	π	π^*	π/π^*	$\Delta\delta$(C14 − C15)
3a, H	1.8122	0.1557	0.0859	7.9
3b, 2-OMe	1.8042	0.1584	0.0878	2, 7
3c, 4-OH	1.8086	0.1721	0.0952	9.6
3d, 4-OMe	1.8071	0.1735	0.0960	10.0
3e, 2,4-OMe	1.7890	0.1769	0.0989	5.0
3f, 4-NMe$_2$	1.7961	0.193	0.1075	13.6
	$\Sigma\pi/\pi^*$	$\frac{\Sigma\pi/\pi^*}{3}$		
3a, H	0.3577	0.1192		
3b, 2-OMe	0.3684	0.1228		
3c, 4-OH	0.3777	0.1259		
3d, 4-OMe	0.3800	0.1267		
3e, 2,4-OMe	0.3931	0.1310		
3f, 4-NMe$_2$	0.4094	0.1365		

however, both *ortho*-substituted compounds **3b** and **3e** deviate, obviously due to steric hindrance forcing the phenyl moiety to be twisted out of the plane of the $C_{14}{=}C_{15}$ double bond. As an indicator of the charge polarization, in other words as a measure of the *push–pull effect*, the effectiveness of $\Delta\delta_{C=C}$ is reduced due to the hindered resonance of $C_{14}{=}C_{15}$ and the donor-substituted phenyl moiety (cf. in Fig. 1 the corresponding correlation).

The *push–pull quotient*, $\pi_{C=C}/\pi^*_{C=C}$,[4] on the other hand, proved to be a reliable indicator for all of the C=C double bonds in **3a–f**. Excellent correlations to the bond lengths for the partial C=C double bonds, $C_6{=}C_9$, $C_4{=}C_5$ and $C_{14}{=}C_{15}$, were obtained (see Fig. 1). Thus, only the *push–pull quotient* fundamentally quantifies the push–pull

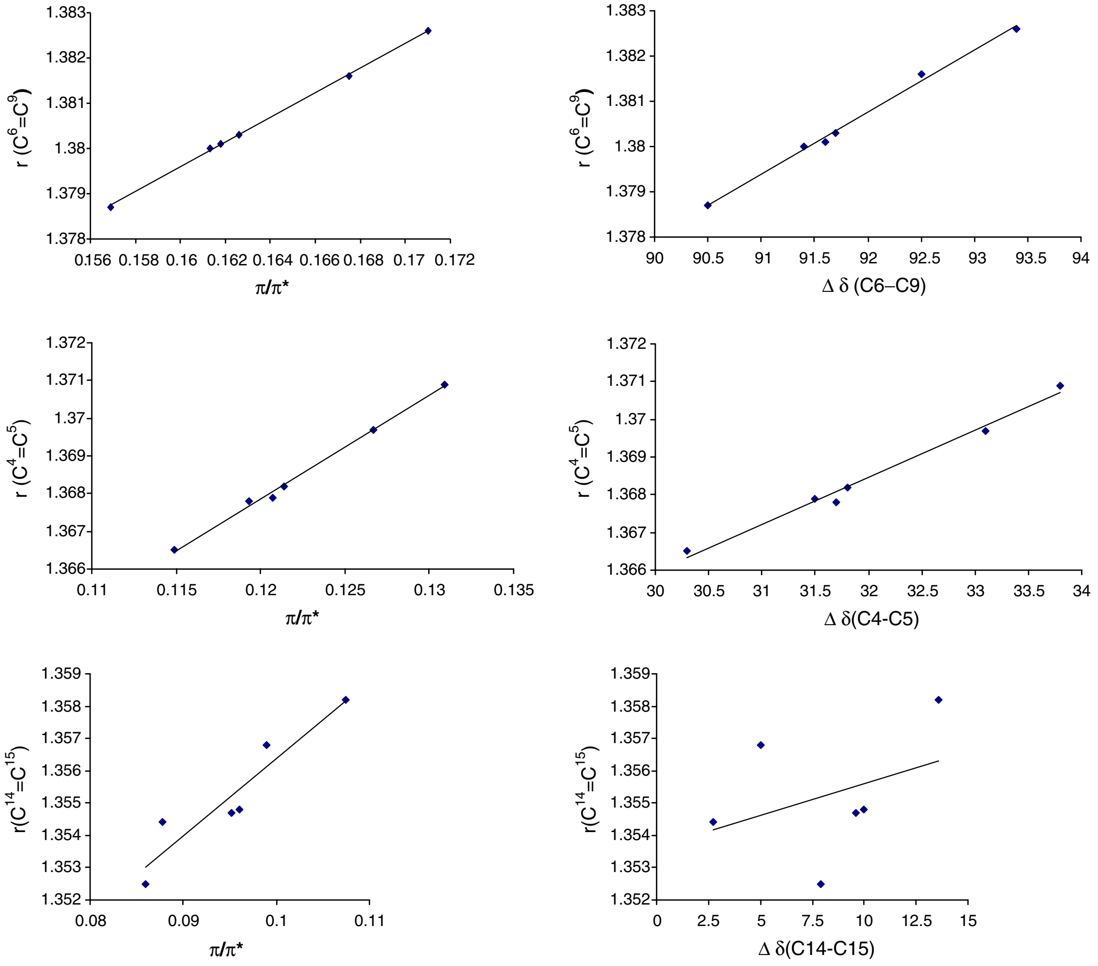


Fig. 1. Correlation of the *push–pull effect* of the $C_6{=}C_9$, $C_4{=}C_5$ and $C_{14}{=}C_{15}$ partial double bonds of isophorone chromophores **3** (π/π^*—left; $\Delta\delta$—right).

character of acceptor/donor–substituted partial C=C double bonds in a general manner. The parameters $\Delta G^{\#}$ and $\Delta\delta_{C=C}$, though proven to be useful in particular cases, are restricted in general cases for indicating the charge polarization present. This is very apparent for the isophorone chromophores **3** with three conjugated C=C double bonds. Thus, even if easily accessible, $\Delta\delta_{C=C}$ is only valid as bond polarization-indicating parameter if the molecular geometry stays planar while the 'push–pull quotient' is still valid but requires NMR measurements to be properly calibrated.

The molecular hyperpolarizabilities at zero frequency $\beta(0)$, contained in Table 2, have been correlated with the mean of the sum of the $\pi_{C=C}/\pi^*_{C=C}$ quotients for all the three C=C double bonds in chromophores **3** (Table 3). A clear linear dependence of the two parameters is apparent (Fig. 2). This thus represents a general structural parameter (the mean *push–pull effect* of the three conjugated partial C=C double bonds) in the isophorone chromophores **3** that correlates with the hyperpolarizability for these compounds. It is important to have an inherent parameter for assessing compounds as suitable NLO materials. Alternatively, the BLA, a parameter usually employed in discussing NLO property–structure relationships[20] due to structural changes, can also be employed along series **3a**–**f**. However, our recommendation is that the *push–pull*

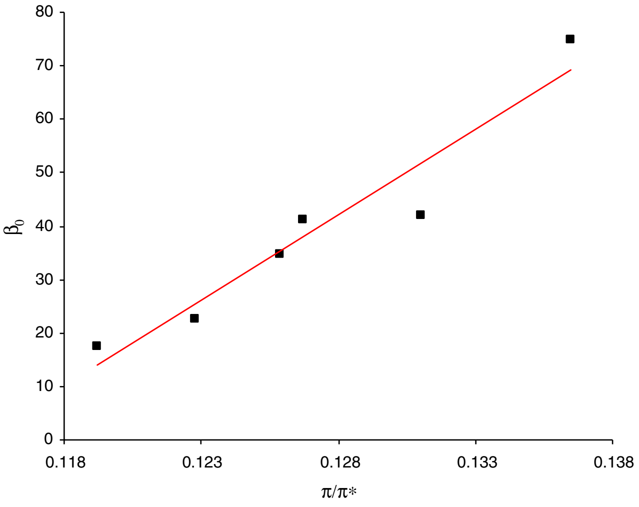


Fig. 2. Correlation of the molar hyperpolarizability of isophorone chromophores **3** with the mean *push–pull effect* of the three partial C=C double bonds present in **3**.

quotient, $\pi_{C=C}/\pi^*_{C=C}$, be employed in characterizing the molecular hyperpolarizabilities of any compounds considered potentially useful as NLO materials. But the molar hyperpolarizability—characterized readily by the present structural parameters of chromophore **3**—is not the only desirable property for new organic NLO materials; there are molecules of better hyperpolarizabilities,[12a] and superior processing capabilities (e.g., sufficient thermal stability during melt growth) for current state-of-the-art materials.[12]

3. Experimental

Chromophores **3** were synthesized by Knoevenagel condensations according to literature procedures[16] and the structures confirmed by ^1H and ^{13}C NMR (see Table 1). Ab initio MO calculations and natural bond orbital (NBO) population analysis[21] were performed using GAUSSIAN 03.[22] Geometry optimizations were performed at the B3LYP/6-311G** level of theory without constraints.[23] Molecular hyperpolarizabilities at zero frequency were calculated using the same model chemistry and the default parameters provided by the '*polar=enonly*' GAUSSIAN 03 key word. Both the size of the basis set and the inclusion of diffuse functions were found to be of negligible influence on the quality of the correlations.

Acknowledgements

B.S. and B.M. thank the Deutsche Forschungsgemeinschaft (DFG) for financial support whilst Dr. Karel D. Klika is thanked for language correction of the manuscript.

References and notes

1. Sandström, J. *Top. Stereochem.* **1983**, *14*, 83.
2. Fischer, G.; Rudorf, W.-D.; Kleinpeter, E. *Magn. Reson. Chem.* **1991**, *29*, 204.
3. (a) Kleinpeter, E.; Klod, S. *J. Org. Chem.* **2004**, *69*, 4317; (b) Kleinpeter, E.; Thomas, St.; Uhlig, G.; Rudorf, W.-D. *Magn. Reson. Chem.* **1993**, *31*, 714.
4. Kleinpeter, E.; Schulenburg, A. *Tetrahedron Lett.* **2005**, *46*, 5995.
5. (a) Benassi, R.; Bertarini, C.; Hilfert, L.; Kempter, G.; Kleinpeter, E.; Spindler, J.; Taddei, F.; Thomas, St. *J. Mol. Struct.* **2000**, *520*, 273; (b) Benassi, R.; Bertarini, C.; Kleinpeter, E.; Taddei, F.; Thomas, St. *J. Mol. Struct. (THEOCHEM)* **2000**, *498*, 201.
6. Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; p 227.
7. Osaka, H.; Ishida, T.; Nogami, T.; Yamazaki, R.; Yasui, M.; Iwasaki, F.; Mizuguchi, A.; Kubata, M.; Uemiya, T.; Nisjimuru, A. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 918.
8. Mahanalingam, K.; Nethaji, M.; Das, P. K. *J. Mol. Struct.* **1996**, *378*, 177.
9. Favini, G.; Gamba, A.; Todeschine, R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 915.
10. Inoue, S.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1997**, 1105.
11. Fabian, W. M. F.; Dworczak, R.; Junek, H.; Pawar, B. N. *J. Chem. Soc., Perkin Trans. 2* **1995**, 903.
12. (a) Cheng, Y.-J.; Luo, J.; Hau, St.; Bale, D. M.; Kim, T.-D.; Shi, Z.; Lao, D. B.; Tucker, N. M.; Tian, Y.; Dalton, L. R.; Reid, Ph. J.; Jen, A. K.-Y. *Chem. Mater.* **2007**, *19*, 1154; (b) Kwon, O.-P.; Ruiz, B.; Choubey, A.; Mutter, L.; Schneider, A.; Jazbinsek, M.; Gramlich, V.; Günter, P. *Chem. Mater.* **2006**, *18*, 4049.
13. Sochova, S. L.; Akella, A.; Hesselink, L. *Opt. Lett.* **1997**, *22*, 919.
14. Wortmann, R.; Lundquist, P. M.; Twieg, R. J.; Geletneky, C.; Moylan, C. R.; Jia, Y.; DeVoe, R. G.; Burland, D. M.; Bernal, M.-P. *Appl. Phys. Lett.* **1996**, *69*, 1657.
15. Van Steenwinckel, D.; Hendricks, E.; Persoons, A. *J. Chem. Phys.* **2001**, *114*, 9557.
16. (a) Lemke, R. *Chem. Ber.* **1970**, *103*, 1894; (b) Lemke, R. *Synthesis* **1974**, 359; (c) Ermer, S.; Lovejoy, S. M.; Leung, D. S.; Warren, H.; Moylan, C. R.; Twieg, R. J. *Chem. Mater.* **1997**, *9*, 1437; (d) Chun, H.; Moon, I.; Shin, D. H.; Kim, N. *Chem. Mater.* **2001**, *13*, 2813.
17. (a) Kolev, Ts. M.; Yancheva, D. Y.; Stamboliyska, B. A. *Spectrochim. Acta Part A* **2003**, *59*, 3325; (b) Ivanova, B. B. *Spectrochim. Acta Part A* **2006**, *65*, 1035.
18. (a) Kolev, Ts. M.; Glavcheva, Z.; Yancheva, D.; Schürmann, M.; Kleb, D. Chr.; Preut, H.; Bleckmann, P. *Acta Crystallogr., Sect. E* **2001**, *57*, o561; (b) Kolev, Ts. M.; Glavcheva, Z.; Schürmann, M.; Kleb, D. Chr.; Preut, H.; Bleckmann, P. *Acta Crystallogr., Sect. E* **2001**, *57*, o1166; (c) Kolev, Ts. M.; Schürmann, M.; Kleb, D. Chr.; Preut, H.; Spiteller, M. *Acta Crystallogr., Sect. E* **2002**, *58*, o1172.
19. Compound **3f** was also examined by dynamic NMR spectroscopy since this chromophore proved to be the strongest polarized of the set and was thus expected to exhibit exchange phenomena. Unfortunately, despite going down to −150 °C (in $CClF_3$) and up to +150 °C (in DMSO-d_6), both the ^1H and ^{13}C NMR signals retained their original line widths. Obviously, barriers to rotation about the $C_6=C_9$ and $C_{14}=C_{15}$ bonds are too high and about C_4–C_{14} and C_{15}–C_{16} are too low to be studied on the NMR timescale and thus dynamic NMR spectroscopy was unable to be utilized in this instance.
20. Champagne, B.; Kirtman, B. In *Handbook of Advanced Electronic and Photonic Materials and Devices*; Nalwa, H. S., Ed.; Nonlinear Optical Materials; Academic Press, 2001; Vol. 9, p 63.
21. Bohmann, J. A.; Weinhold, F.; Farrar, T. C. *J. Chem. Phys.* **1997**, *107*, 1173.
22. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M.; Farkas, C. O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, C. S.; Ochterski, J.; Petersson, G. A.; Ayala, P.; Cui, Y. Q.; Morokuma, K. D.; Malick, K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, L.; Gomperts, R.; Martin, L. R.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98 (Revision A.12); *Gaussian*: Pittsburgh PA, 2002.
23. Hehre, J. W.; Radom, L.; von, R.; Schleyer, P.; Pople, J. A. In *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.