Arylaldehydes-pentafluorophenyl Hydrazones as Second-order Nonlinear Optical Chromophores: A Novel Approach for Remarkably Defeating the Nonlinearity-transparency Trade-off

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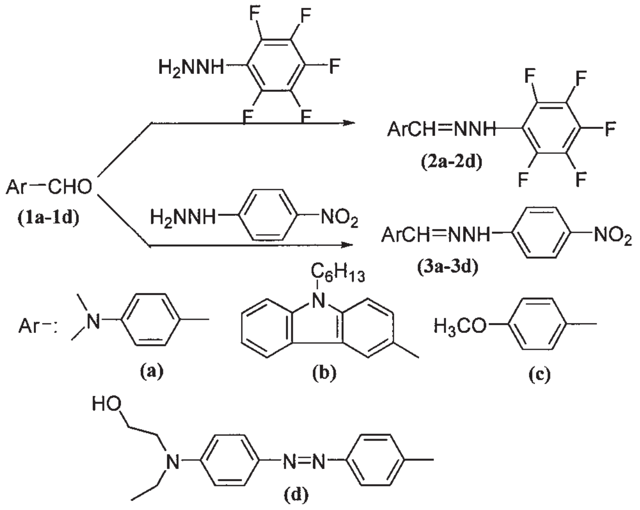
A series of new arylhydrazone chromophores containing pentafluorophenyl as electronic acceptor are synthesized and found to exhibit significantly blue-shifted absorption in comparison with the corresponding 4-nitrophenyl analogues while keeping β value in the same order, and this may provide a new opportunity for defeating nonlinearity-transparency trade-off in designing second-order nonlinear optical chromophores.

Organic second-order nonlinear optical (NLO) materials have been the subject of intense investigations owing to their exceptionally large nonlinearity and ultrafast response times.[1] These materials have potential applications in areas such as telecommunications, optical information processing and data storage.[2] One of the major challenges in this research is to design and synthesize second-order NLO chromophores possessing simultaneously large first-order molecular hyperpolarizability (β), high thermal stability and good transparency.[3] To date, most highly nonlinear optical second-order chromophores have been constructed by following the "π-donor linked to π-acceptor through a π-backone" prescription. An intriguing question, however, centers around the possibility of using modification in the "NLO-inactive" σ-framework to indirectly affect the "NLO-active" π-system. Electronegative fluorine substituted systems, that are weak π-donors and strong σ-acceptors, could serve as such prototypical moieties. ZINDO-SOS theoretical calculation results strongly suggest that so-called inductive acceptors can be used to produce highly efficient chromophores and the β values of the chromophores containing pentafluorophenyl acceptor are approximately half as potent as those with a 4-nitrophenyl acceptor.[4]

Recently, Alain reported that push-pull diphenylpolyenes with a trifluoromethyl acceptor moiety can offer promising opportunities in terms of transparency-efficiency trade-off and have a particular interest for applications based upon cascading processes.[5] Jen also reported that the incorporation of this type of chromophores based on the α-perfluoroaryldicyanovinyl electron acceptors into polyquinoline led to both high electro-optical property and low optical loss.[6] On the other hand, Zyss et al. have reported[7] that 1,3-diphenylhydrazones, which exhibit similar transparency and larger static first-order hyperpolarizability β_0 as compared to the corresponding diene derivatives, offer a slight improvement of the nonlinearity-transparency trade-off. Here, we report the first synthesis and their β values of a series of new arylhydrazone chromophores (**2a-2d** in Scheme 1) with pentafluorophenyl as an electron acceptor.

Four arylaldehydes-pentafluorophenyl hydrazones (**2a-2d**) were prepared by the condensation reaction of the corresponding arylaldehydes and pentafluorophenylhydrazine in anhydrous ethanol. We also synthesized the corresponding 4-nitrophenylhydrazone compounds (**3a-3d** in Scheme 1) for the purpose of comparison. The spectral data and the results of elemental analysis for all of the products were consistent with the expected structures.[8]



Scheme 1.

The β values of the chromophores **2a-2d** and **3a-3d** were measured by Hyper-Rayleigh Scattering (HRS) technique[9] in methanol using the fundamental excitation wavelength of 1064 nm. The known β value for p-nitroaniline (p-NA) in methanol (34.5×10^{-30} esu)[10] was used as an external reference. The measured hyperpolarizabilities β and the static β_0 obtained from the two-level modulation of these compounds as well as their absorption maxima (λ_{max}) are given in Table 1.

For a given donor and conjugated bridge, it has been found that the β values of the arylhydrazones with pentafluorophenyl acceptor are similar to those of the corresponding 4-nitrophenyl analogues, and the results are in consistent with the prediction by ZINDO-SOS theoretical calculation.[4] However, it is very interesting to note that **2a-2d** show dramatically blue-shifted absorption when compared with the corresponding 4-nitrophenyl analogues: 87 nm for **2a**; 92 nm for **2b**; 91 nm for **2c**; 32 nm for **2d**. UV-Vis absorption phenomena of **2a-2d** highlight the unusual structure and properties of pentafluorophenyl acceptor and indicate that the pentafluorophenyl group as the electron acceptor give rise to better transparency.

On the other hand, by comparison of **3a** with 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS) and 4-(*N*,*N*-dimethylamino)-4′-nitroazobenzene (DANAB), it can be seen that transparency of **3a** is similar to that of DANS but better than that of DANAB, while their β_0 values are comparable. The hydrazones

Table 1. Optical properties of **2a-2d** and **3a-3d**

Chromophores	λ_{max}/nm in methanol	β^a (10^{-30} esu) at $\lambda = 1064$ nm	$\beta_0{}^c$ (10^{-30} esu)
2a	344	161	84
3a	431	329	95
2b	331	112	62
3b	423	147	46
2c	319	64	37
3c	410	165	57
2d	439	199	53
3d	471	279	55
DANAB	474	97^b	55^d
DANS	438^e	73^b	42^d
p-NA	370	34	16

$^a\beta$ values measured by HRS technique in methanol using the fundamental excitation wavelength of 1064 nm. $^b\beta$ measured by EFISH in chloroform using the fundamental excitation wavelength of 1300 nm.[10] ^{c,d}Dispersion-corrected β values calculated by using an approximate two-level model (d see Reference 10). ^{e}Measured in chloroform.

seem then to offer interesting nonlinearity-transparency compromise as compared to the corresponding stilbene and azobenzene derivatives. In addition, **2a-2c** exhibited also 26–51 nm blue-shifted absorption in comparison with p-NA, and their β values are 2–5 times higher than that of p-NA. All the above results suggest that arylhydrazone chromophores with pentafluorophenyl moieties exhibit better optimization of the nonlinearity-transparency trade-off.

In summary, we have synthesized a series of new arylhydrazone chromophores containing pentafluorophenyl as electron acceptor. They all show remarkablely blue-shifted absorption in comparison with the corresponding 4-nitrophenyl analogues and provide a new approach for turning the nonlinearity-transparency trade-off.

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8 The yield, melting point, IR (KBr, cm^{-1}), NMR (300 MHz), MS, and elemental analysis data for these compounds are as follows: **2a:** yield 86%; mp 171–172 °C ; IR 1666 (-C=N), 3352 (N-H); ^{1}H-NMR ($CDCl_3$) δ 2.99(s, 6H), 6.69(d, J = 9.0, 2H), 7.03(s, 1H), 7.51(d, J = 9.0, 2H), 7.74(s, 1H); MS(FAB), *m/z*: 329, 100%. Anal. Calcd for $C_{15}H_{12}N_3F_5$: C, 54.71; H, 3.64; N, 12.76%. Found: C, 55.02; H, 4.15; N, 12.85%. **2b:** yield 89%; mp135–136 °C; IR 1662(C=N), 3317(N-H); ^{1}H-NMR ($CDCl_3$) δ 0.84(t, 3H), 1.32(m, 6H), 1.86(m, 2H), 4.24(t, 2H), 7.28–7.36(m, 4H), 7.72–7.84(m, 2H), 7.88(s, 1H), 8.08(s, 1H), 8.24(s, 1H); MS(FAB), *m/z*: 459, 100%. Anal. Calcd for $C_{25}H_{22}N_3F_5$: C, 65.36; H, 4.79; N, 9.15%. Found: C, 65.15; H, 4.95; N, 8.75%. **2c:** yield 73%; mp 120–121 °C; IR 1664(-C=N), 3358 (N-H); ^{1}H-NMR ($CDCl_3$) δ 3.84(t, 3H), 6.91(d, J = 9.0, 2H), 7.15(s, 1H), 7.56(d, J = 9.0, 2H), 7.78(s, 1H); MS(FAB), *m/z*: 316, 100%. Anal. Calcd for $C_{14}H_9F_5N_2O$: C, 53.16; H, 2.84; N, 8.86%. Found: C, 53.45; H, 3.15; N, 8.85%. **2d:** yield 79%; mp 193–194 °C; IR 1664(-C=N), 3242(N-H); ^{1}H-NMR(DMSO) δ 1.12(t, 3H), 3.34(m, 6H), 6.76(d, 2H), 7.60–7.76(m, 6H), 8.10(s, 1H), 10.4(s,1H); MS(FAB), *m/z*: 477, 100%. Anal. Calcd for $C_{23}H_{20}F_5N_5O$: C, 57.86; H, 4.19; N, 14.67%. Found: C, 57.45; H, 4.55; N, 14.85%. **3b:** yield 81%; mp 151–152 °C; IR 1359, 1540(-NO_2), 3253(N-H); ^{1}H-NMR ($CDCl_3$) δ 0.85(t, 3H), 1.31(m, 6H), 1.88(m, 2H), 4.34(t, 2H), 6.99(d, 1H), 7.18–7.53(m, 4H), 7.92–8.03(m, 2H), 8.09–8.21(m, 4H), 8.62(s, 1H), 10.09(s, 1H); MS(FAB), *m/z*: 414, 100%. Anal. Calcd for $C_{25}H_{26}N_4O_2$: C, 72.46; H, 6.28; N, 13.52%. Found: C, 72.25; H, 6.31; N, 13.35%. **3d:** yield 76%; mp 197–198 °C; IR 1340, 1522 (-NO_2), 3238 (N-H); ^{1}H-NMR (DMSO) δ 1.12(t, 3H), 3.12(m, 4H), 3.52(t, 2H), 6.76(d, J = 10, 2H), 7.16(d, J = 10, 2H), 7.68–7.76(m, 6H), 8.04–8.12(d, 2H), 8.16(s, 1H), 11.32(s, 1H); MS(FAB), *m/z*: 432, 100%. Anal. Calcd for $C_{23}H_{24}N_6O_3$: C, 63.89; H, 5.56; N, 19.44%. Found: C, 63.45; H, 5.75; N, 19.25%.

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