Heterocyclic Azole Nonlinear Optical Chromophores. 1. Donor–Acceptor Substituted Pyrazole Derivatives

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We have described the synthesis of a variety of 1,3, 1,4, and 1,5 donor–acceptor conjugation extended substituted pyrazole derivatives and have studied their spectroscopic and nonlinear optical properties. These materials are thermally stable and absorb strongly in the UV–visible region, albeit at much shorter wavelengths than comparably substituted cyclic azapolyenes such as 2-pyrazolines. Quadratic hyperpolarizability measurements suggest that the pyrazoles are significantly nonlinear, and that 1,3 and 1,4 substitution is preferred. 1,5 substitution causes a significant drop in the nonlinearity and a blue shift in the long-wavelength absorption maximum, presumably due to a twisting and partial deconjugation of the substituents to relieve unfavorable steric interactions. The experimental results are compared with those predicted by simple "finite field" computational procedures.

Introduction and Background

Organic materials are potentially interesting nonlinear optical (NLO) materials because of their large intrinsic nonlinearities, rapid response times, high radiation damage thresholds, low dielectric constants, and ease of fabrication.[1-4] Chromophores which show large second-order nonlinearities are usually unsymmetrically substituted, with both electron-donating and electron-accepting groups separated by a molecular spacer capable of mediating the electronic interaction between the substituents. These molecular spacers are most often π-conjugated systems such as olefins, acetylenes, and aromatic groups, etc., although there are recent reports of significantly nonlinear chromophores where the substituent interaction is mediated by σ-conjugation in silicon catenates.[5-7] In classical π-conjugated chromophores, the effectiveness of the substituents is often predictable based on consideration of the appropriate resonance substituent constants (σ_R, $\sigma^{+/-}$, etc.)[8-10] derived from linear free energy relationships even though the Hammett constants[11,12] are influenced only by ground-state properties whereas the hyperpolarizabilities depend on excited-state properties as well. While resonance interactions usually dominate the effect, inductively attracting moieties can be useful substituents.[2,13,14]

Most donor–acceptor substituted NLO chromophores are characterized by a long-wavelength charge-transfer transition that dominates the nonlinearity and hence contributes strongly to the second-order molecular hyperpolarizability. The molecular hyperpolarizabilities of such systems are often successfully described by a two-state model[15,16] in which

$$\beta_0 = \beta_\omega\left(1 - \frac{\lambda_{\max}{}^2}{\lambda^2}\right)\left(1 - 4\frac{\lambda_{\max}{}^2}{\lambda^2}\right) \qquad (1)$$

β_0, defined by eq 1, is interpreted as the intrinsic molecular hyperpolarizability of the chromophore extrapolated to zero frequency, independent of resonance effects caused by the proximity of the electronic absorption to either the laser fundamental or the second harmonic. Experimentally, β_0 can be estimated from the measured quadratic polarizability by knowing the chromophore absorption maximum ($\lambda_{\max}$) and the laser fundamental wavelength as shown in eq 1. Recent theoretical studies have suggested that maximization of β_0 requires simultaneous consideration of the donating and accepting powers of the substituents in conjunction with the nature of the electronic spacer.[17] The frequency correction factor is derived for the two-state model and is accurate only if the model is appropriate for the particular chromophore under investigation.

Aromatic rings are particularly popular as conjugating substituents because of their thermal and oxidative stability, synthetic availability, and substituent positional

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selectivity. Although materials of this type often have lower intrinsic nonlinearities than those containing catenated olefinic and acetylenic linkages, the blue-shifted absorptions and particularly the thermal and oxidative stability of aromatic substituents make them attractive for many potential device applications. For example, the construction of high-frequency electrooptic switches and phase and amplitude modulators and their integration into semiconductor devices plase additional demands on the NLO materials beyong their intrinsic nonlinearity.[18-20] For integrated optoelectronic switching or modulation, a device might need to withstand continuous operating temperatures of 80–100 °C, as well as brief excursions to 250 °C or more which are often associated with current semiconductor processing. A key component of polymeric NLO materials is the chromophore, which can be incorporated by a variety of techniques (host-guest arrays, tethered attachment, main-chain incorporation, etc.). The induction and maintenance of polar order in such devices under actual device operating conditions, however, remains a serious concern. Equally important for high temperature applications, the polymer–chromophore system must be thermally stable and must not degrade under environmental influences. With this in mind, we have commenced a study of a number of thermally stable, substituted heterocyclic azole chromophores. In this paper we describe our studies on a variety of donor–acceptor substituted pyrazoles where the conjugation pathway between the substituents is maintained via the nonbonding electrons of the substituted, trivalent heterocyclic ring nitrogen atom.

Although substituted six-membered aromatic derivatives of benzene, pyridine, and their polycyclic and conjugatively extended analogues have been widely studied as NLO chromophores,[2,4,10,21] limited data have been accumulated for five-membered heterocyclic azole derivatives such as imidazoles, oxadiazoles, oxazoles, thiazoles, pyrazoles, and their benzannulated derivatives.[2,22-24] These materials, which provide a thermally stable, planar, quasi-aromatic framework, are readily available in a variety of substituent types and patterns.

Azole derivatives containing a trivalent nitrogen (e.g., pyrrole, imidazole, pyrazole, 1,2,4-triazole, etc.) provide an additional potential bonding site. In these systems, attachment of substituents to both the trivalent nitrogen and an appropriate ring carbon can provide a fully conjugated system utilizing the nitrogen unshared electron pair. Under these circumstances, the heterocyclic ring itself also becomes a significant electron-donating substituent.[25]

The pyrazole ring system is a thermally and oxidatively stable, quasi-aromatic representative of the broader general class of five-membered heterocyclic azole derivatives.[26,27] Simple comparisons of both the empirical resonance energy and conjugation energy of pyrazole with those of pyrrole and imidazole predict that the former is considerably more aromatic.[28] However, more recent LCAO-SCF calculations suggest that (i) in the azole series the stability decreases with increasing substitution of nitrogen for carbon, and (ii) the aromatic stabilities of pyrazole and imidazole are comparable.[29] Regardless of the computational details, it is apparent that by all theoretical and experimental criteria, pyrazole derivatives possess the enhanced stability normally associated with aromatic character.

Semiempirical calculations on compounds containing a nitrogen lone pair as part of a conjugated system suggest that chromophores of this type should be substantially nonlinear.[30,31] As a result, it has been suggested that 1,3-disubstituted 4,5-dihydro-1*H*-pyrazoles (2-pyrazolines) should constitute an interesting class of NLO chromophores. Stimulated by this interesting prediction, Allen et al.[32,33] have reported the synthesis and characterization of the crystalline, strongly nonlinear, donor–acceptor substituted 2-pyrazoline, 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-4*H*-pyrazole, a material whose measured electrooptic coefficient (r_{33}) was 87 pm/V. While the 2-pyrazolines may show large nonlinearities, they also have certain drawbacks for some applications. First, they are oxidatively labile with the quasi-aromatic stability of the resulting pyrazole providing a significant driving force. Second, 1,3 donor–acceptor substitution in a 2-pyrazoline results in highly colored materials. For example, the dicyanoethenyl derivative described above absorbs strongly at 466 nm.[32] Even 1,3-diphenyl-2-pyrazoline itself absorbs at 363 nm.[34] The strong visible absorptions limit the utility of donor–acceptor substituted pyrazolines for such applications as second harmonic generation at fundamental wavelengths shorter than $\sim 1.06\ \mu$m and even electrooptic applications require a judicious tradeoff between operation at shorter wavelengths in the spectral region of highest NLO efficiency and the deleterious effects caused by heating and optical loss due to chromophore light absorption.

The impressive thermal and oxidative stability of substituted pyrazoles, coupled with their synthetic accessibility, unusual spectroscopic properties, and the demonstrated nonlinearity of a number of simple crystalline derivatives[35] led us to a detailed study of the quadratic molecular polarizabilities of this interesting class of azole derivatives.

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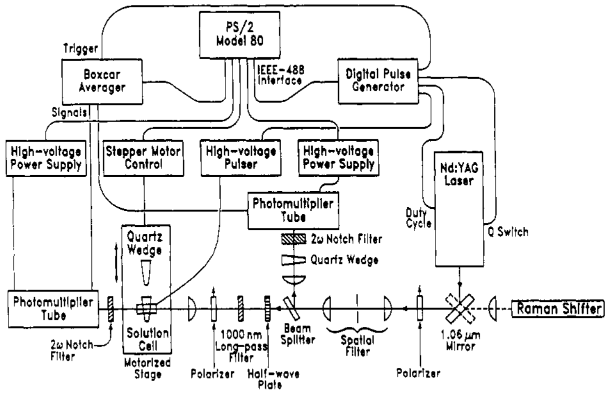

Figure 1. Schematic of apparatus used for EFISH measurements.

Experimental Section

UV spectra were recorded using a Hewlett-Packard 8452A diode array instrument and are therefore accurate to ±2 nm. Reaction solvents were routinely dried prior to use and UV solvents were spectroscopic grade. The *p*-dioxane used for the characterization experiments was spectral grade and was used without purification. Dioxane was selected as the solvent because of its good solvent properties and low dipole moment. Measurements were performed immediately after the samples were prepared. Some variation in the results was observed if the dioxane solutions were allowed to stand for extended periods before measurement. All precursors as well as the pyrazoles themselves were prepared and characterized as described by Miller and Reiser.[36] The structures were consistent with all spectroscopic and analytical data. The structure of **3c** was also verified by single-crystal X-ray analysis.

Molecular hyperpolarizabilities were measured using the electric field-induced second harmonic technique (EFISH).[15,37-39] In this technique, a solution of the chromophore being studied fills the small gap between two wedged glass windows held between upper and lower electrodes of a high-voltage cell. The voltage across the electrodes is pulsed to approximately 8 kV for 20 μs, and a spatially filtered pulse of 1.064-μm light from a Spectra-Physics DCR-3G Nd:YAG laser is focused through the cell coincident with the electrical pulse. The 1.064-μm light that emerges from the cell is filtered, and the remaining 532-nm light is detected by means of a photomultiplier tube. A similar PMT detects frequency doubled light by a reference quartz sample, so that the signal can be normalized and pulse-to-pulse variation in laser intensity is compensated. The triangular solution cell is scanned with respect to the optical path, so that the laser path length through the solution steadily increases. The resulting interference pattern yields the signal amplitude (from the height of the peaks) and the coherence length (from the spacing of the peaks). Amplitudes and coherence lengths were recorded for each chromophore concentration. Concentrations used ranged from 0.5 to 5 wt %. The experimental apparatus is shown in Figure 1.

Dielectric constants[40] of all solutions at 1 MHz were determined using a home-built solution capacitance cell and a Hewlett-Packard Model 4284A LCR meter. From these data, the concentration dependence of the dielectric constant was determined. The EFISH data were combined with the known indexes of refraction, density, and dielectric constant of the solvent, as well as the known susceptibilities of the glass windows and reference quartz wedge, to yield the infinite dilution limit of the concentration dependence of the solution susceptibility.[41] The equations, constants and conventions used for data analysis are described in detail in ref 42. This quantity was combined with the concentration dependence of the dielectric constant, using mixed Onsager-Debye local field factors, to yield an experimental third-order susceptibility Γ. In our calculations, the concentration dependence of n^2 and specific volume were assumed to be negligible; in general, they contribute only a few percent to Γ.

The effective third-order coefficient is actually the sum of terms involving both the second- and third-order polarizabilities β and γ:[43]

$$\Gamma = \gamma + \frac{\mu\beta}{5kT} \tag{2}$$

In this work, we have neglected the γ contribution. The β values given in the following sections thus represent upper limits.

To determine β from Γ, the dipole moment of the chromophore must be determined, which was accomplished as follows. The concentration dependence of the solution dielectric constant was used as an approximation for the quantity

$$\frac{(\epsilon - n^2) - (\epsilon_0 - n_0^{\,2})}{C} \tag{3}$$

using again the assumption that the concentration dependence of n^2 is small. The Guggenheim expression[44] for the dipole moment can thus be rewritten as

$$\mu = \sqrt{\frac{27kT}{4\pi N_0(\epsilon_0 + 2)(n_0^{\,2} + 2)}\left(\frac{\partial\epsilon}{\partial C}\right)} \tag{4}$$

Values of $\lambda_{\max}$ obtained from the UV-vis spectra were used to extrapolate β (1.064 μm) to zero frequency (β_0) according to the two-state model[15,16] using eq 4.

For comparison purposes, a general figure of merit Q is introduced, equal to $10^{43}\mu\beta_0/\lambda_{\max}$ in cgs units. β_0 is chosen to represent the intrinsic nonlinearity of the compound; μ measures how easily it can be oriented to take advantage of its nonlinearity; and $\lambda_{\max}$ is a rough indicator of the molecule's transparency. A figure of merit specific to second harmonic generation would depend on $(\lambda_{\max})^{-2}$, whereas one specific to electrooptical would not have an inverse $\lambda_{\max}$ dependence at all. Because the EFISH experiment yields the product of the dipole moment and the hyperpolarizability, using that quantity in the figure of merit ensures that the uncertainity in the dipole moment value makes no contribution to the uncertainity in Q.

Results

Synthesis. Although there are many synthetic routes to pyrazole derivatives, the vast majority involve the condensation of substituted hydrazines with a variety of β-dicarbonyl derivatives or equivalents.[26,27] Since we were interested primarily in the preparation of donor–acceptor substituted pyrazoles, often containing conjugation extending substituents, many of the classical techniques either lacked generality or required exotic starting materials. For this reason, we chose to study the cyclocondensation of aryl and substituted cinnamoyl-α,β-acetylenic ketones with appropriately substituted and readily available phenylhydrazine derivatives.[36] Scheme I describes this procedure as applied to the synthesis of 1,3- and 1,5-disubstituted pyrazole derivatives. The ratio of the isomeric pyrazole products can be controlled to some extent by the choice of reaction conditions. Using this procedure, a wide variety of aryl- and β-styryl-substituted pyrazole derivatives may be prepared, a number of which are listed in Table I.

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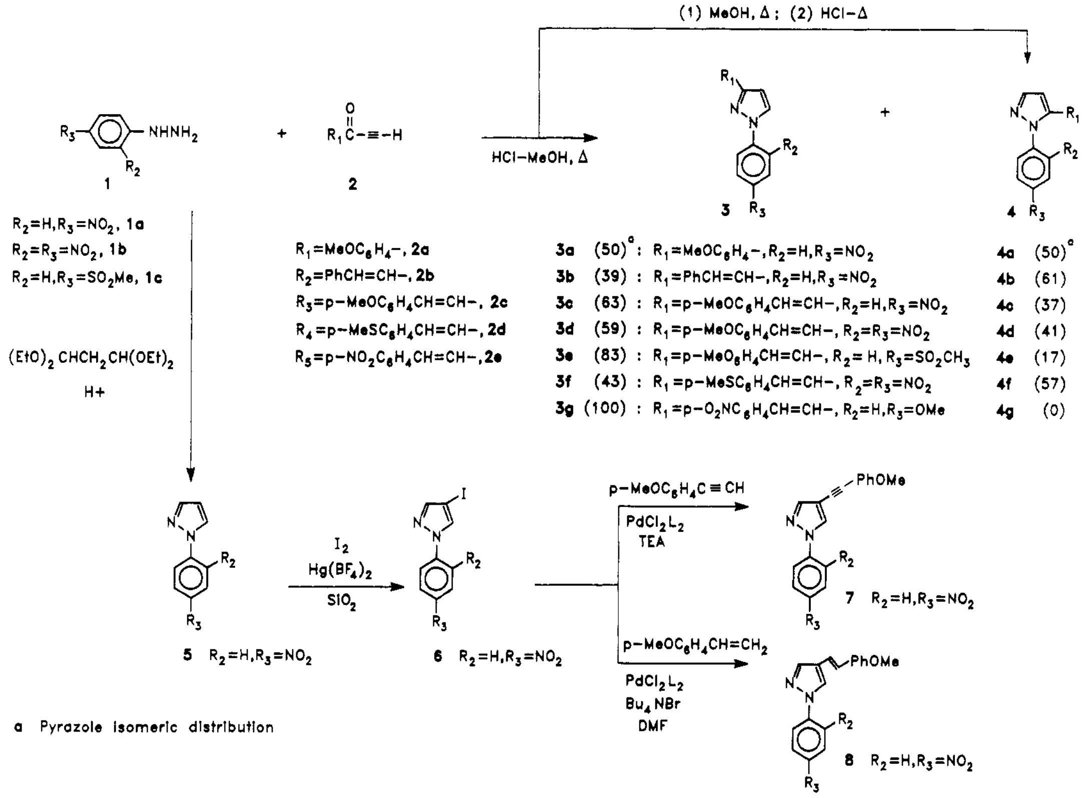
Scheme I. Synthesis of Disubstituted Pyrazoles



a Pyrazole isomeric distribution

Table I. Properties of a Variety of Aryl- and Styryl-Substituted Pyrazoles

entry	pyrazole	mp, °C	λ_{max} (ε),[a] nm
1	**3a**: R_1 = $MeOC_6H_4$, R_2 = H, R_3 = NO_2	197–198	352 (16 736)[b]
2	**4a**	101–103	296 (9 750)[b]
3	**3b**: R_1 = PhCH = CH–, R_2 = H, R_3 = NO_2	184–186	346 (32 720)
4	**4b**	138–140	298 (28 142)
5	**3c**: R_1 = p-$MeOC_6H_4CH{=}CH$–, R_2 = H, R_3 = NO_2	178–180	364 (34 900)[c]
6	**4c**	154–156	302 (28 819)
7	**3d**: R_1 = p-$MeOC_6H_4CH{=}CH$–, R_2 = R_3 = NO_2	178–180	375 (19 286)[c]
8	**4d**	171–173	306 (28 867)
9	**3e**: R_1 = p-$MeOC_6H_4CH{=}CH$–, R_2 = H, R_3 = SO_2Me	233–235	328 (33 706)[c]
10	**4e**	179–181	326 (21 962)
11	**3f**: R_1 = p-$MeSC_6H_4CH{=}CH$–, R_2 = H, R_3 = NO_2	150–153	354 (31 373)
12	**4f**	177–179	312 (31 719)
13	**3g**: R_1 = p-$O_2NC_6H_4CH{=}CH$–, R_2 = H R_3 = OMe	159–161	370 (26 688)[c]
14	**7**: R_2 = H, R_3 = NO_2	170–172	340 (21 267)
15	**8**: R_2 = H, R_3 = NO_2	230–232	358 (21 434)

[a] Measured in p-dioxane unless otherwise noted. [b] Ethanol. [c] Acetonitrile.

The preparation of 1,4-disubstituted derivatives requires a different synthetic approach that utilizes the tendency of many N-substituted pyrazoles to undergo electrophilic substitution specifically in ring position 4.[26,27] Using this technique, 4-bromo- and 4-iodo-1-(p-nitrophenyl)pyrazole can be prepared isomerically pure and in good yield. Although the former is formed spontaneously upon treatment with Br_2, the latter requires the use of an activating catalyst such as mercuric tetrafluoroborate absorbed on silica gel. Surprisingly, the bromide was inert to palladium-catalyzed carbon–carbon bond formation under the general conditions described by Hagihari[45,46] and Heck[47] for acetylenes and olefins, respectively. The more reactive iodide, however, underwent a variety of palladium-catalyzed coupling reactions to yield the desired 4-β-styryl- and 4-phenylethynyl-substituted pyrazoles **8** and **7** also described in Scheme I. All of the derivatives reported in Table I are colored, highly crystalline materials readily soluble in organic solvents. For the preparation of 1,3- and 1,5-disubstituted derivatives, the isomeric ratios (noted in Scheme I by the numbers in parentheses) in the crude reaction product depend strongly on the experimental conditions. The overall pyrazole yields range from 45 to 90%. The melting points and the positions of the long-wavelength UV absorption maxima for each individual isomer are also listed in Table I.

Measurements. The quadratic molecular polarizability (β_ω) of each pyrazole was measured in p-dioxane solution by the EFISH technique as described above.[42,48] The measured values for β_ω, β_0, and the dipole moments for the pyrazole derivatives are reported in Table II. In a study of the nonlinearity–transparency tradeoff for the pyrazoles, log β_0 was plotted vs the log of λ_{max} of the long-wavelength absorption, and the result is shown in Figure 2.

Calculations. Simple "finite field"[49-51] MOPAC hyperpolarizability calculations were performed on a variety of aryl- and β-styryl-substituted pyrazoles using the

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Table II. Molecular Hyperpolarizability Measurements on a Variety of Substituted Pyrazoles by Electric Field Induced Second Harmonic Generation (EFISH)

entry	pyrazole	λ_{max},[a] nm	μ,[a] D	$10^{30}\beta$[a,b] esu	$10^{30}\beta_0$, esu	Q[c]
1	**3a**	354	6.6	31.4	15.6	29.0
2	**4a**	306	6.3	12.7	7.8	16.1
3	**3b**	346	6.1	32.2	16.6	29.4
4	**4b**	298	4.6	7.3	4.6	7.2
5	**3c**	368	5.7	40.1	18.4	28.5
6	**4c**	302	5.5	13.6	8.5	15.5
7	**3e**	330	5.6	15.6	8.7	14.8
8	**3f**	354	4.1	41.6	20.6	23.8
9	**4f**	312	3.3	11.5	6.9	7.2
10	**3g**	370	7.0	48.2	21.9	41.4
11	**7**	340	5.6	20.0	10.6	17.4
12	**8**	358	5.1	63.3	30.7	43.5

[a] Measured in *p*-dioxane solution. [b] Measured at laser fundamental of 1.06 μm. [c] $Q = 100\ \mu\beta_0 \times 10^{30}/\lambda_{max}$ nm.

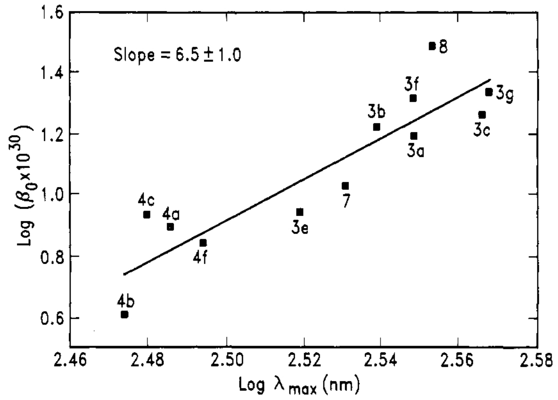

Figure 2. Nonlinearity–transparency tradeoff for substituted pyrazoles in dioxane.

PM3[52,53] technique. The calculated dipole moments and intrinsic molecular hyperpolarizabilities are reported in Table III. The calculations were first performed on the planar structures, where the appropriate torsional angles were fixed to maintain maximum overlap between the interacting π and nonbonding orbitals while permitting the optimization of other structural parameters. The corresponding numbers in the parentheses refer to geometry minimized structures calculated without restraints.

Discussion

Pyrazole derivatives are synthetically accessible and thermally and environmentally stable and absorb at considerably shorter wavelengths than comparably substituted 2-pyrazolines. For example, the λ_{max} for 1,3-diphenylpyrazole occurs at 278 nm,[54] strongly blue-shifted from the comparable pyrazoline[34] ($\Delta\bar{\nu}$ = 8038 cm^{-1}). When substituted on nitrogen at position 1, the pyrazole ring itself becomes a significant electron-donating substituent. In this respect, σ_p resonance substituent constants ranging between 0.19 and 0.24 have been measured for the pyrazole moiety by IR and ^{1}H NMR techniques.[25] These values are similar to those of halogen substituents such as Cl, Br, and I. Furthermore, judicious substitution at appropriate ring carbons of the pyrazole nucleus can further increase the electron donating capacity.

Recent studies of simple 1-nitrophenyl-substituted pyrazole derivatives suggest that these compounds may be potentially interesting NLO materials,[35] particularly where nonlinearity–transparency issues are important. In this regard, a number of simple substituted, crystalline 1-(*p*-nitrophenyl)pyrazoles have been demonstrated to be 9–16 times more effective than urea for second harmonic generation as assessed by the Kurtz powder test. To our knowledge, however, the intrinsic quadratic molecular polarizabilities of even simple substituted pyrazole derivatives have not been studied.

The synthetic procedures elaborated in Scheme I allow the preparation of a wide variety of donor–acceptor substituted pyrazoles derivatives, including materials where the conjugation path has been significantly extended. The synthetic availability of 1,3-, 1,4-, and 1,5-substituted derivatives allows a detailed study of the effects of substitution type and position on the molecular hyperpolarizabilities.

As shown in Scheme I, 1,3- and 1,5-disubstituted derivatives are prepared by cyclocondensation of α,β-acetylenic ketones with readily available substituted phenylhydrazines. The pyrazole isomeric ratio in mixtures is conventiently controlled simply by varying the reaction conditions. The procedure is widely applicable for the synthesis of a variety of alkyl-, aryl-, and styryl-substituted derivatives. Reaction of α,β-acetylenic ketones with substituted phenylhydrazines in neutral media followed by the addition of acid leads exclusively to 1,5-disubstituted pyrazoles. Detailed mechanistic studies have shown that in the absence of acid, the initial reaction involves the Michael addition of the primary amino group of the phenylhydrazine to the terminal acetylenic carbon followed by cyclization in the presence of acid.[36] In contrast, if acid is present from the onset, a mixture of 1,3- and 1,5-disubstituted derivatives often results. As a result of mechanistic studies, the acid-catalyzed route has been described by competitive 1,2- and 1,4-addition of the hydrazine to the carbonyl derivative followed by the regioselective cyclization of the respective intermediates. 1,4-Disubstituted derivatives are available by palladium-catalyzed carbon–carbon bond formation to the precursor 4-halopyrazole derivatives. Since position 4 is the favored site for electrophilic substitution of the pyrazole ring under all but the most strongly acidic conditions, these derivatives are readily prepared by halogenation of the preformed substituted pyrazole. While 1-(nitrophenyl)-4-iodopyrazole is not produced directly upon treatment of 1-(nitrophenyl)pyrazole with iodine, it is the only product generated by iodination in the presence of mercuric tetrafluoroborate absorbed on silica gel.[55] The active electrophilic species in this procedure is believed to be iodine tetrafluoroborate.

All of the pyrazoles discussed in this paper are reasonably high melting (Table I), crystalline solids thermally stable to 200 °C or above (as determined by thermal analysis techniques) which absorb strongly in the UV–visible spectral region. The solution UV absorption maxima of the longest wavelength transition are also reported in Table I. The UV absorption spectra are not solvatochromic in a manner anticipated for materials expected to show a long-wavelength charge-transfer transition.[56–58] For ex-

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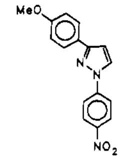
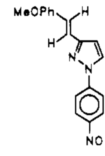
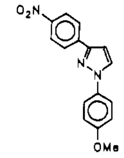
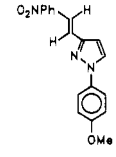
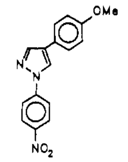
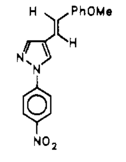
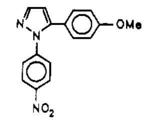
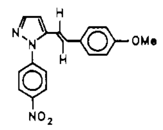
Table III. Finite Field Hyperpolarizability Calculations Using MOPAC-PM3

entry	structure	μ, D	$10^{30}\beta_0$, esu	entry	structure	μ, D	$10^{30}\beta_0$, esu
1		4.7[a]	29.7[a]	5		4.8 (5.6)	38.3 (31.5)
2		8.7[a] (8.8)[b]	10.4[a] (10.1)[b]	6		8.9 (8.7)	21.9 (20.8)
3		5.3 (5.5)	24.0 (21.9)	7		5.3 (5.4)	30.1 (29.2)
4		5.8 (5.4)	12.9 (8.6)	8		5.3 (4.7)	16.0 (11.6)

[a] Planarized structure. [b] Geometry minimized by the program.

ample, the λ_{max}'s for **3a** and **3c** are actually slightly *blue* shifted (4–5 nm) upon increase in the solvent polarity from benzene to highly polar media such as ethanol or acetonitrile.

Examination of the data in Table I shows that the donor–acceptor substituted pyrazoles absorb at wavelengths much shorter than comparably substituted 2-pyrazolines. For example, **3a** absorbs strongly at 352 nm while the absorption of 1-(*p*-nitrophenyl)-3-(*p*-methoxyphenyl)-2-pyrazoline occurs at 441 nm.[30] Even the conjugation extended derivative **3c** absorbs at relatively short wavelengths (λ_{max} 364 nm). In this study, the pyrazole with the longest wavelength absorption was the dinitro derivative **3d** (λ_{max} 375 nm).

A number of other conclusions can be drawn from the UV data in Table I. Styryl substitution leads to red shifts in absorption versus the simple diaryl pyrazoles, but only to the extent of 900–1200 cm^{-1}. The molar extinction coefficients measured at the absorption maxima seem also to increase somewhat with conjugation extension. Exchange in the positions of donor-acceptor substitution (e.g., **6c** vs **3g**) seems to have little effect on the absorption spectra. This was somewhat unexpected based on studies of similarly substituted 2-pyrazolines where the difference in the absorption maxima between 1-(*p*-nitrophenyl)-3-(*p*-methoxyphenyl)pyrazoline and the positional isomer 1-(*p*-methoxyphenyl)-3-(*p*-nitrophenyl)-2-pyrazoline is more than 2500 cm^{-1}.[30] There is also relatively little difference between the position of the long-wavelength absorption maxima of 1,3-styryl-substituted pyrazoles **3b–g** and the 1,4-substituted derivative **8**. Phenylethynyl substitution (e.g., **7**) does, however, result in a significant blue shift of the absorption relative to that of the styryl derivative **8**. Similar shifts have been reported for donor–acceptor substituted tolanes relative to comparably substituted stilbene derivatives.[10,59] The absorption spectra of these latter derivatives are often significantly solvatochromic,[48] unlike the corresponding pyrazole derivatives.

Finally, all of the 1,5-disubstituted pyrazoles **4a–g** absorbed at *much* shorter wavelengths than either comparably substituted 1,3 or 1,4 derivatives. In the case of 1,5 substitution, at least some of this difference can be attributed to twisting of the substituents to minimize the steric interactions between the groups. Related spectral effects on other substituted pyrazoles have been previously observed.[54,60,61] Consistently, PM3 geometry minimization calculations on 1,5-diaryl- and 1-aryl-5-β-styryl-substituted pyrazoles suggest that both substituent groups are significantly twisted. This effect is further exacerbated when the tetrahedral nitrogen is planarized to permit optimal overlap between the interacting π orbitals and the nitrogen lone pair.

Quadratic molecular polarizabilities and dipole moments of the pyrazole derivatives are reported in Table II. The pyrazoles studied here have substantial ground state dipole moments, a result consistent with the simultaneous presence of strong electron donor and acceptor substituents interacting via an extended conjugated system.[40] In each case, the measured dipole moments for 1,3 substitution were somewhat larger than for the 1,5-substituted isomers. The quadratic molecular polarizabilities measured at 1.06 μm were significantly resonance enhanced and were reduced by approximately a factor of 2 by applying the frequency correction factor based on the two-state model. This enhancement is due primarily to the proximity of the optical absorption to the second harmonic generated at 532 nm.

Comparison of the zero-frequency molecular polarizabilities (β_0) in Table I shows that all of the pyrazoles derivatives have respectable nonlinearities. In a number of cases the values for β_0 are comparable to or exceed that

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measured for 4-methoxy-4′-nitrostilbene ($\beta_0 = 23 \times 10^{-30}$ esu, based on a frequency-corrected value measured at 1.91-μm laser fundamental frequency),[10] a significantly nonlinear chromophore. As expected, for comparable substitution, extension of the conjugation path (β-styryl vs aryl) increased the molecular hyperpolarizability somewhat (e.g., **3a** vs **3c**), although the difference is not overwhelming and is accompanied by an increase in the λ_{max} for the long-wavelength absorption. For styryl substitution in position 3, the presence of a sulfur group in the para ring position only slightly increases the β_0 value over the oxygen derivative (entries 5 vs 8). Surprisingly, interchange of the donors and acceptors (entries 5 vs 10) results in a relatively small change both in the respective absorption spectra as well as in the values for β_0. This result is quite different from that predicted by CNDO/S type calculations on 1,3-disubstituted-2-pyrazolines[31] which suggest that materials with donor substituents in position 1 and acceptors in position 3 not only should absorb at longer wavelengths but also should have substantially improved nonlinearities. For the pyrazoles, similar substituent position dependent hyperpolarabilities were also predicted based on simple "finite field" calculations performed on substituted derivatives (vide infra).

As anticipated, replacement of the nitrophenyl group by a poorer electron accepting substituent in position 1 (e.g., $-PhSO_2Me$ vs $-PhNO_2$) resulted in both a significant blue shift in the absorption maximum and a substantial drop in the measured nonlinearity (entries 5 vs 9). Donor substitution in either positions 3 or 4 of the pyrazole ring led to large molecular hyperpolarizabilities for both isomers, although substitution in the latter position seems somewhat more effective. Furthermore, for 1,4-substituted pyrazoles, changing the substituent in position 4 from *p*-alkoxy-β-styryl to (*p*-alkoxyphenyl)ethynyl (entry 12 vs 11) resulted in both a blue-shifted absorption maximum and a significantly lower nonlinearity. Finally it should be noted that 1,5-substitution in the pyrazole ring leads to substantially lower nonlinearities than for comparably substituted 1,3 and 1,4 derivatives. This is presumably due, at least in part, to partial disruption of the conjugation and to the twisting of the aryl substituents caused by unfavorable steric interactions.[54,60,61]

As discussed previously for other conjugated systems, for the pyrazoles there appears to be a relationship between the intrinsic nonlinearity (β_0) and the long-wavelength absorption maximum.[10,62-64] Figure 1 shows a plot of log β_0 vs log λ_{max} for *p*-dioxane solvent. Although there is admittedly some scatter in the data, the slope of the least-squares line drawn through the points is 6.5 ± 1.0, a value intermediate between those reported for substituted benzenes (4.4)[10] and stilbenes (~9.3).[10] On the basis of this analysis, it seems that β_0 for the substituted pyrazoles varies as $\lambda_{max}{}^n$ where n is approximately 6.5.

Finally, simple "finite field" hyperpolarizability calculations on a variety of substituted pyrazoles have been performed using the PM3 procedure within the commercially available MOPAC computational package. The results of the calculations shown in Table III pertain specifically to calculations in the gas phase and are intended for relative comparison only rather than for direct comparison of the absolute magnitudes with experimental results obtained by the EFISH measurements in solution.[65] In the calculations on the *p*-methoxstyryl derivative (entry 5), two localized planar geometry minima were found which differed in the orientation of the 3-substituent by a 180° rotation around the single bond joining the group to the ring. The calculated heats of formation and the hyperpolarizabilities for each form were quite similar. We have selected the form shown in Table III, since it corresponds to that found in the single-crystal X-ray structure of **3c**.[66]

Inspection of the numbers in Table III leads to a variety of predictions. Calculations predict that the quadratic molecular polarizabilities for donor–acceptor substituted pyrazoles should be substantial, as confirmed by experiment. For comparable substituent groups, the calculations also suggest that extension of the conjugation pathway by replacing a simple aryl substituent with the appropriate β-styryl group should lead to an increase in the respective molecular hyperpolarizabilities. This is found to be the case also in the experimental measurements.

The calculated quadratic hyperpolarizabilities were large for both 1,3 and 1,4 substitution. This was also found to be the case in the experimental studies, although the measured values for the latter were somewhat larger than the former for comparable substitution (Table II entries 5 and 12). Calculations also correctly predict that the hyperpolarizabilities for both 1,3 and 1,4 substitution should be considerably larger than for 1,5 substitution. This is true even for 1,5 derivatives which have been fixed planar in spite of the strong steric interactions which would normally lead to a twisting of the substituents. This result suggests an intrinsically lower β_0 value for 1,5 substitution, an effect further exacerbated by any twisting of the aromatic rings to relieve unfavorable steric interactions. This prediction is also borne out by experiment, although the importance of the intrinsic electronic effects relative to those caused by substituent twisting cannot be separated.

For comparably substituted 1,3 and 1,5 derivatives, the calculations suggest that twisting of the electron-attracting group has a much greater effect on the calculated hyperpolarizabilities than rotation of the electron-donating substituents. This effect is presumably due to the fact that the pyrazole moiety itself is a respectable electron-donating substituent when bonded through nitrogen to an electron-attracting substituent.[31]

Finally, it should be noted that the finite field calculations predict that both the dipole moment and the hyperpolarizabilities should be sensitive to the relative order of polar attachment for 1,3-substitution. For example, the studies suggest that a pyrazole derivative with a donor substituent bonded to N1 and an acceptor bonded to C3 should have a higher dipole moment but a significantly lower quadratic polarizability than the alternative bonding arrangement. While the former prediction is consistent with the experimental data, the latter is not, at least for the single pair of examples that were compared experimentally (see Table II entries 5 and 10).

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(65) For a discussion on the comparison of calculated and experimental quadratic polarizabilities see ref 42 and: Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.*, in press.

(66) X-ray structure of **3c**: monoclinic, space group $P2_1/C$ (No. 14). Lattice parameters: a = 20.162 Å, b = 7.340 Å, c = 21.786 Å, β = 106.929 Å.

Further experimental and computational studies of substituent positional effects on the hyperpolarizabilities of substituted azole chromophores is proceeding.

Conclusions

We have described the synthesis of a variety of thermally stable, donor–acceptor, conjugation-extended substituted pyrazole NLO chromophores and studied their spectroscopic and NLO properties. The synthetic procedures allow the facile synthesis of a number of 1,3-, 1,4-, and 1,5-disubstituted derivatives. These materials are not significantly solvatochromic and absorb strongly in the UV–visible region, albeit at much shorter wavelengths than comparably substituted conjugated cyclic azapolyenes such as the 2-pyrazolines, etc. While the spectral properties of 1,3- and 1,4-disubstituted pyrazoles are similar, comparably substituted 1,5 derivatives absorb at much shorter wavelengths, presumably due to substituent twisting in the latter to avoid unfavorable steric interactions.

Similar effects are observed for the quadratic hyperpolarizabilities of the pyrazoles, with the measured values being large for 1,3 and 1,4 substitution and dramatically lower for the 1,5-substituted derivatives. Limited comparison of the nonlinearities of 1,3- and 1,4-substituted pyrazoles seem to suggest that the latter pattern is preferred. As expected, conjugation extension improves the nonlinearity for all substitution patterns. For 1,3-disubstitution there seems to be little effect of the position of polar attachment on the molecular hyperpolarizabilities, in contrast to simple theoretical predictions.

Comparison of the nonlinearity-transparency issue for the substituted pyrazoles suggests that the frequency independent quadratic polarizabilities vary with $\lambda_{\max}{}^{n}$, where $n \sim 6.5$, a value intermediate between donor–acceptor substituted benzene and stilbene derivatives. The high thermal and environmental stability of donor–acceptor substituted pyrazoles in conjunction with their large molecular hyperpolarizabilities and favorable spectral properties suggests a potential utility for NLO applications either in the crystalline state or as incorporated chromophores in poled-polymer media.

Supplementary Material Available: Crystallographic characterization data for **3c** (42 pages); list of calculated and observed structure factors (31 pages). Ordering information is given on any current masthead page.