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Synthesis, Vapor Growth, Polymerization, and Characterization of Thin Films of Novel Diacetylene Derivatives of Pyrrole. The Use of Computer Modeling To Predict Chemical and Optical Properties of These Diacetylenes and Poly(diacetylenes)

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Abstract: In the present work two diacetylene derivatives of pyrrole (compounds **1** and **2**), which are predicted by semiempirical AM1 calculations to have very different properties, are synthesized; the polymerizability of these diacetylenes in the solid state is determined; and the results are compared to the computer predictions. Diacetylene **1** is novel in that the monomer is a liquid at room temperature; this may allow for the possibility of polymerization in the liquid state as well as the solid state. Thin poly(diacetylene) films are obtained from compound **1** by growing films of the monomer using vapor deposition and polymerizing with UV light; these films are then characterized. Interestingly, while the poly(diacetylene) from **1** does not possess good nonlinear optical properties, the monomer exhibits very good third-order nonlinear optical effects (e.g., phase conjugation) in solution. Dilute acetone solutions of the monomer **1** give intensity-dependent refractive indices (n_2) on the order of 10^{-6} esu ($\chi^{(3)}$ values on the order of 10^{-7} esu); these are 10^6 times better than for CS_2.

Introduction

Poly(diacetylenes) have shown great promise as third-order nonlinear optical materials for applications such as optical switching and four-wave mixing.[1] Generally, these compounds are prepared by growing thin crystalline films of diacetylene monomers using vapor deposition and then polymerizing the films in the solid state by exposure to UV light or γ-radiation.[2] The preparation of poly(diacetylenes), however, is not a trivial matter. The synthesis of diacetylenes typically requires several steps involving very reactive compounds, and often products are obtained in low yields. Also, polymerization of diacetylenes to give crystalline poly(diacetylenes) is typically a solid-state process[3] and, unfortunately, it is impossible to predict whether or not a crystalline diacetylene monomer will polymerize. Furthermore, diacetylenes usually crystallize as needles, cubes, or lozenges, whereas thin crystalline films are most useful for nonlinear optical applications. Formation of good quality crystalline films of the monomers is not always straightforward,[4-6] and even if a good monomer film is obtained, it may not readily polymerize. Lastly, there is no guarantee that the poly(diacetylene) film produced will have good nonlinear optical properties.

Because of the above-mentioned difficulties, we have investigated the use of computer modeling as a means of screening potentially interesting compounds.[3,7] One does not wish to spend months in the laboratory synthesizing and growing thin films of a diacetylene, only to discover that it does not polymerize well, or that the polymer does not have good nonlinear optical properties. Thus computer models that could predict the chemical and optical properties of diacetylenes and poly(diacetylenes) would be of great value. Currently, the best computer modeling method makes use of semiempirical molecular orbital calculations such as PM3, MNDO, and AM1.[8-10] These models attempt to predict how diacetylene monomers will pack in a crystal, which is critical in determining whether or not they will polymerize readily. Additionally, computations yield HOMO–LUMO bandgaps, which are a major factor in predicting the optical properties of poly(diacetylenes).

In the present work, AM1 calculations are used to predict the chemical and optical properties of two diacetylene derivatives of pyrrole, compounds **1** and **2**. These two compounds, although they differ only by a CH_2 group, are predicted to have very different

Table I. Crystal Packing Parameters Calculated by AM1 for Some Diacetylene Monomers[a]

$XC{\equiv}CC{\equiv}CY$

compd	X	Y	d (Å)	θ (deg)
1	*N*-pyrrolylmethyl	hydroxymethyl	8.52	37
2	*N*-pyrrolyl	hydroxymethyl	5.42	60
3	hydrogen	hydrogen	6.75	25
4	hydrogen	chlorine	6.05	46
5	chlorine	chlorine	5.95	50
6	methyl	methyl	5.48	47
7	methyl	hydrogen	6.60	45
8	hydrogen	methoxy	6.05	48
9	hydroxymethyl	hydroxymethyl	5.85	55
10	2-hydroxyethyl	2-hydroxyethyl	5.75	50
11	acetyl	acetyl	5.50	66
12	1-hydroxyethyl	1-hydroxyethyl	5.55	45
13	phenyl	phenyl	7.30	55
14	methyl	propargyl	8.40	30
15	*N*-pyrrolyl	*N*-pyrrolyl	5.20	57
16	*N*-pyrrolylmethyl	*N*-pyrrolylmethyl	5.70	66
17	*N*-carbazolyl	hydroxymethyl	6.50	56
18	*N*-methylacetamido	*N*-methylacetamido	4.97	50
19	*N*-carbazolylmethyl	hydroxymethyl	8.05	40

[a] Reference 7.

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(1) Heeger, A. J., Ulrich, D. R., Eds. *Nonlinear Optical Properties of Polymers*; North Holland Press: New York, 1988.

(2) Wegner, G. *Z. Naturforsch.* **1969**, *246*, 824.

(3) Jalali-Heravi, M.; McManus, S. P.; Zutaut, S. E.; McDonald, J. K. *Macromolecules* **1991**, *24*, 1055. Jalali-Heravi, M.; Zutaut, S. E.; McManus, S. P.; McDonald, J. K. *Polym. Prepr.* (*Am. Chem. Soc. Div. Polym. CHem.*) **1991**, *32* (1), 78.

(4) Sandman, D. J., Ed. *Solid State Polymerization*; American Chemical Society: Washington, DC, 1987.

(5) For application of vapor transport growth, see: McManus, S. P.; Patel, D. N.; McDonald, J. K. *Prog. Pac. Polym. Sci., Proc. Pac. Polym. Conf., 1st* **1989**, *207*, (1).

(6) Langmuir–Blodgett techniques are applicable to monomers which have hydrophobic and hydrophilic ends, and various special techniques such as melt processing have been used in some cases; cf: Ulrich, D. R. In *Nonlinear Optical and Electroactive Polymers*; Prasad, D. N., Ulrich, D. R. Eds.; Plenum: New York, 1988; pp 1-11.

(7) McManus, S. P.; Zutaut, S. E.; et al. Manuscript in preparation.

(8) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4870.

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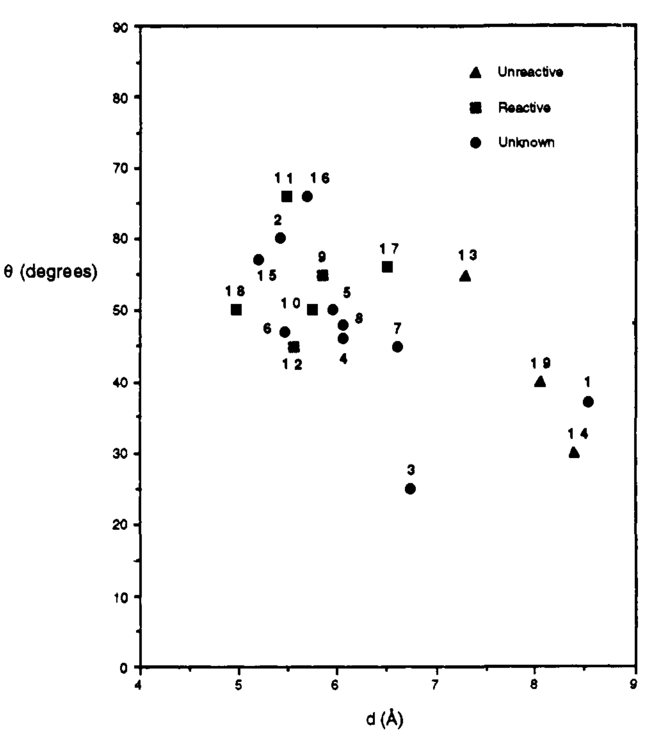
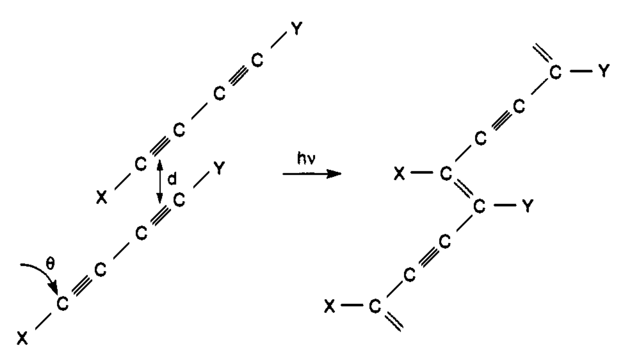


Figure 1. Plot of crystal packing parameters calculated by AM1 for several diacetylenes, including some compounds reactive for solid-state polymerization, some unreactive, and some unknown (see Table I).[7]

properties. The purpose of this work is to synthesize compounds **1** and **2**, grow thin films of the monomers by vapor deposition, polymerize the films in the solid state by UV radiation, characterize the resulting poly(diacetylene) films (i.e., determine their third-order nonlinear optical properties), and see how the results compare to the computer predictions. The nonlinear optical properties of the monomer **1** are also investigated.

Methods and Results

Computer Modeling. AM1 calculations were carried out on several diacetylenes (Table I), including some known compounds which have previously been characterized, as well as some unknown compounds (including, at the time, compounds **1** and **2**). A detailed discussion of these and other semiempirical molecular orbital calculations on diacetylenes and their polymers will be treated in a forthcoming publication.[7] Estimates of crystal packing parameters were calculated for each diacetylene using geometry-optimized monomer pairs. Because of the linear structure of the diacetylene moiety of the molecules, the crystal structure can essentially be described in terms of two parameters: the stacking distance, d, between monomers and the angle, θ, between the diacetylene rod and the stacking axis (see drawing). When these two parameters are plotted against each other for the compounds in Table I, the scatter graph shown in Figure 1 results. Note a very interesting feature of the graph: all of the compounds which are known to polymerize readily in the solid state tend to be grouped together in one area of the graph, while those which do not polymerize readily lie outside this area. This could provide the desired predictive tool for the solid-state polymerizability of diacetylene monomers. The result seems reasonable since it is known that diacetylene polymerization in the crystal is a topochemical process and, thus, occurs readily only when neighboring monomer molecules are sufficiently close together and are oriented suitably.[2] Since only a certain range of values of d and θ would satisfy this requirement, all of the diacetylenes which polymerize readily in the solid state should be expected to occur in the same region of the graph.



HOMO–LUMO bandgaps for the diacetylene monomers were also computed using AM1; these can provide some indication of the optical properties of the polymers.[7] The smaller the bandgap, the more red shifted the edge of the absorption band becomes. The size of the bandgap is also a measure of the degree of conjugation between the diacetylene backbone and the pendant groups (X and Y). This has a direct effect on the nonlinear optical properties; generally, a small bandgap means more conjugation and hence better nonlinear optical properties.

In order to further test the predictive utility of the computer model, it was decided to select two unknown compounds which, according to the AM1 calculations, should have very different properties, and see how experimental results compare to the predictions. It is clear from Figure 1 that diacetylene **1** falls well outside the reactive area for polymerization, whereas diacetylene **2** lies well within the reactive area. Thus, although they differ only by a CH_2 group, compound **1** should not polymerize readily in the solid state, but compound **2** should. The bandgaps for the monomers **1** and **2** are calculated by AM1 to be 8.86 and 8.98 eV, respectively;[7] these nearly equal values suggest that the poly(diacetylenes) obtained from **1** and **2** probably differ little in their optical properties. Intuitively, we expect that the poly(diacetylene) from **2** might have better nonlinear optical properties than that from **1** because, unlike that from **1**, there exists the possibility of conjugation between the pyrrole ring of compound **2** and the poly(diacetylene) backbone (this, however, depends on the conformation of the molecule; effect conjugation requires that the pyrrole ring be coplanar with the poly(diacetylene) backbone, which may not necessarily be the case). Matsuda and others have described the preparation of cross-conjugated poly(diacetylenes), which were shown to have optical properties superior to similar polymers without the cross-conjugated groups directly attached to the backbone.[11] The goal of the present work is to determine how compounds **1** and **2** actually behave in view of these predictions.

Synthesis and Properties. The synthesis of compounds **1** and **2** is based on a procedure by Matsuda et al. for making the carbazole analogue of **2** (compound **17** in Table I, also known as CPDO).[11] The method is essentially the Chodkiewicz and Cadiot coupling of the two halves of the diacetylenes, which themselves have to be synthesized.[12] The synthetic schemes for compounds **1** and **2** are outlined herein (Scheme I).

3-Bromopropargyl alcohol is made by a variation of a procedure for preparing bromophenylacetylene.[13] *N*-Propargylpyrrole is prepared by the method of Cantor and Vanderwerf; because of its reactivity, it is kept refrigerated and handled under nitrogen.[14] The coupling of these two reagents to produce compound **1** proceeds straightforwardly; the diacetylene is purified by column chromatography on silica gel using benzene as the eluent. Even purified samples of the monomer **1** possess a reddish-brown color due to the presence of small amounts of polymer (oligomer). This

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(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(10) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

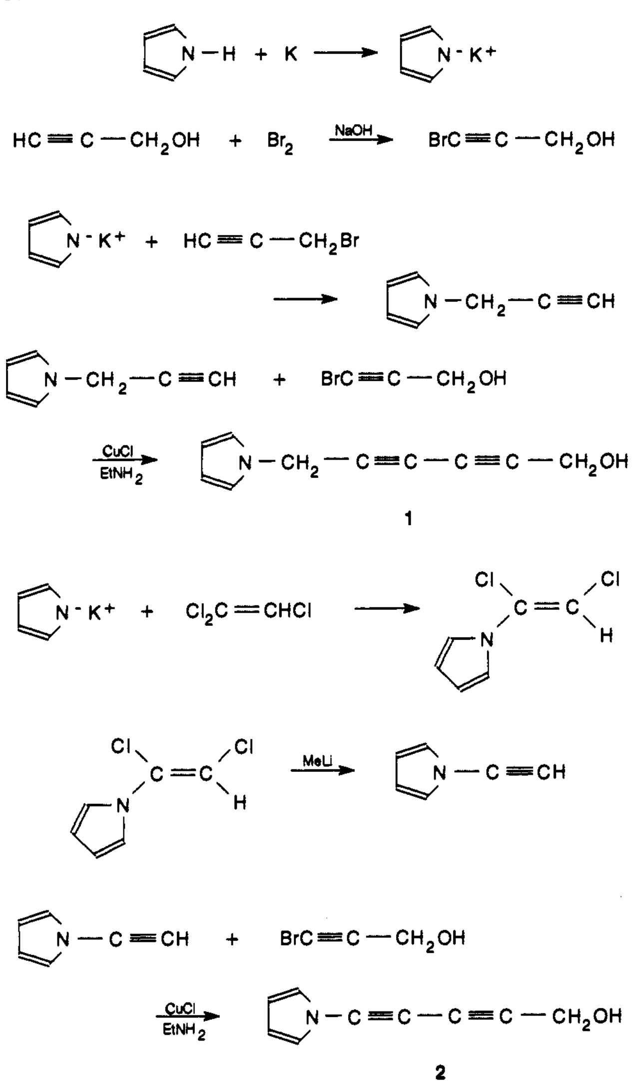
(11) Matsuda, H.; Nakanishi, H.; Hosomi, T.; Kato, M. *Macromolecules* **1988**, *21*, 1238. Matsuda, H.; Nakanishi, H.; Minami, N.; Kato, M. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 241.

(12) Chodkiewicz, W.; Cadiot, P. *C. R. Hebd. Seances Acad. Sci.* **1955**, *241*, 1055.

(13) Miller, S. I.; Zeigler, G. R.; Wieleseck, R. *Organic Syntheses*; Wiley: New York, **1973**, Collect. Vol. *5*, 921.

(14) Cantor, P. A.; Vanderwerf, C. A. *J. Am. Chem. Soc.* **1958**, *80*, 970.

Scheme I



compound is also kept refrigerated and stored under nitrogen.

Interestingly, diacetylene monomer **1** exists as a liquid at room temperature (its freezing point is around 5 °C). This result is quite novel since essentially all diacetylenes previously studied for nonlinear optics have been solids at room temperature.[15] Hence there exists the possibility that this diacetylene could be polymerized in the liquid state as well as the solid state. It would be interesting to compare the two methods; some of the limitations (mentioned in the Introduction) which apply to solid-state polymerization of diacetylenes might not apply to liquid-state polymerization. On the other hand, the poly(diacetylene) chains formed in the liquid state would probably be less ordered and thus may have inferior optical properties. In future work we shall investigate this further. Solid-state polymerization of compound **1** is discussed below.

The synthesis of diacetylene **2** requires that we first obtain *N*-(α,β-dichlorovinyl)pyrrole and *N*-ethynylpyrrole, both of which are previously unknown compounds. The synthesis of *N*-(α,β-dichlorovinyl)pyrrole was achieved using a procedure that was developed for the preparation of α,β-dichlorovinyl ethyl ether from trichloroethylene; pyrrole anion was substituted for ethoxide anion, and the desired product was obtained.[16] *N*-Ethynylpyrrole was then obtained from *N*-(α,β-dichlorovinyl)pyrrole using the general method of Ficini and Barbara for the synthesis of aminoacetylenes from (α,β-dichlorovinyl)amines.[17] Methyllithium in ether was used in place of *n*-butyllithium in hexane because, with the latter reagent, we found it troublesome to separate both *n*-butyl chloride byproduct and hexane from *N*-ethynylpyrrole (they have similar volatilities); there was no such problem with methyllithium. Like *N*-propargylpyrrole, this compound should be stored refrigerated under nitrogen.

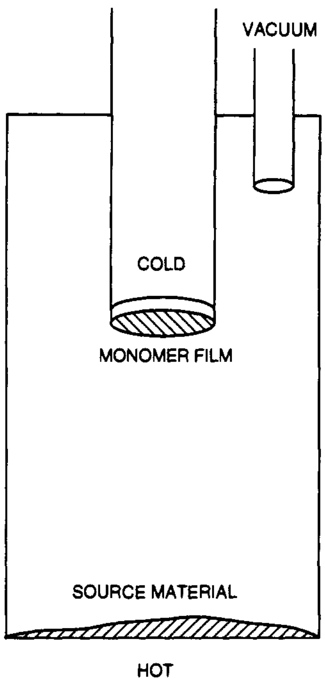


Figure 2. Schematic diagram of the apparatus used to grow thin monomer films of diacetylene **1** by vapor deposition.

The coupling of *N*-ethynylpyrrole with 3-bromopropargyl alcohol (in the dark) to form diacetylene **2** yields a mixture of products (evident from ^{1}H-NMR results). The NMR spectrum of the crude reaction mixture indicates the presence of **2** and/or its polymer (based on comparison with the NMR spectrum of **1**). We have observed that the poly(diacetylenes) give the same NMR spectra as do their monomers, although the peaks are broadened for the polymers (such is the case for **1** and its polymer using acetone as the NMR solvent). Unfortunately, we are unable to isolate monomer **2** from the reaction mixture. Because we are unable to extract any monomer, but do observe compound **2** in the crude reaction mixture, we strongly suspect that the diacetylene monomer forms initially in the reaction and then spontaneously polymerizes (the poly(diacetylene) is not soluble in benzene, which is used to extract the monomer). This result is hardly surprising since the AM1 calculations predict that compound **2** should be very reactive for polymerization. Apparently (from the NMR results), there are also significant side reactions taking place during (or possibly after) the formation of compound **2**.

Vapor Growth and Polymerization. Thin crystalline films of diacetylene monomer **1** can be grown on glass or quartz disks by vapor deposition using a source temperature of 30–32 °C and a condenser temperature of −20 °C at a pressure of 20 μmHg (Figure 2). Although the freezing point of the diacetylene is only 5 °C, a much lower condenser temperature is needed to condense the vapor directly to solid because of undercooling. The resulting polycrystalline diacetylene monomer films are essentially colorless (translucent).

Polymerization of **1** in the solid state is achieved by allowing the monomer film to remain on the condenser (in a nitrogen atmosphere) and exposing the film to a 100-W long-wavelength (365 nm) UV light for about 3 days. Upon exposure to the UV light, the monomer film initially emits a blue fluorescence, which later becomes yellow-green and, finally, orange as the polymerization proceeds. The resulting poly(diacetylene) film, which is

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[15] A possible exception is 2,7-dioxoocta-3,5-diyne (compound **11** in Table I), which we have prepared, but have found to be too reactive for isolation; cf.: McManus, S. P., et al. cited in ref 2.

[16] Crompton, H.; Vanderstichele, P. L. *J. Chem. Soc.* **1920**, *117*, 691.

[17] Ficini, J.; Barbara, C. *Bull. Soc. Chim. Fr.* **1965**, 871.

yellow-brown in color, is then allowed to warm to room temperature (while remaining solid) and can be characterized. These extreme conditions for polymerization are consistent with the computer prediction that compound **1** should be unreactive for polymerization; reactive diacetylenes typically require only a few hours of exposure to a weak UV source.[2]

Characterization. As mentioned above, the poly(diacetylene) films obtained from compound **1** are yellow-brown in color, which is indicative of a significant bandgap and/or poor polymerization (it was not possible to determine the degree of polymerization because the mechanical integrity of the films was too poor to allow the monomer to be washed off without destroying the films). Generally, poly(diacetylenes) which have good optical properties have small bandgaps and are blue or red in color. Thus we do not anticipate good nonlinear optical properties from the polymer films produced from **1**. This is indeed the case when third-order experiments are actually carried out on the films. At 514 nm, using an argon ion laser, there is complete absorption of the laser light (even with thin films). When a Nd:YAG laser with a frequency doubler is used (532 nm), the laser beam burns through the film. These results indicate that the poly(diacetylene) obtained from compound **1** shows little promise as a third-order nonlinear optical material (at least at the laser wavelengths studied here).

Despite the fact that the polymer produced from **1** does not show good nonlinear optical properties, it was decided to investigate the properties of the monomer. Hence third-order experiments were carried out on an acetone solution of diacetylene monomer **1**. Much to our surprise, compound **1** shows very good third-order effects in solution. At 514 nm (argon ion laser) the solution exhibits very good self-focusing and defocusing, as well as self-phase modulation. When the laser beam is passed through the solution and projected onto a screen, multiple diffraction rings (associated with self-phase modulation) can be seen. Similar effects have been observed previously with chinese tea solutions.[18] These results are indicative of intensity-dependent refractive indices (n_2), which, in turn, are indicative of a large third-order nonlinear susceptibility, $\chi^{(3)}$. Additionally, using a frequency-doubled Nd:YAG laser (532 nm), compound **1** exhibits very good phase conjugation in acetone solution, which is further indication of a large $\chi^{(3)}$. The observation of such effects from a diacetylene monomer is very interesting and quite novel; it has somewhat tacitly been assumed that only poly(diacetylenes), because of their highly conjugated chains, could have good nonlinear optical properties.[1]

In order to rule out the possibility that these effects may have resulted from small amounts of polymer (oligomer) impurities present in the monomer, a sample was purified using vapor deposition and the third-order experiments were repeated; the same results as before were obtained. For a solution of compound **1** in acetone (30 mg/mL), the intensity-dependent refractive index, n_2 (at 514 nm), is measured as 3.3×10^{-6} esu; this, in turn, gives a $\chi^{(3)}$ value of 4.8×10^{-7} esu.[19] These values are about 10^6 times greater than those for CS_2, which is a significant result. Because the UV-visible absorption spectrum of compound **1** in acetone shows no absorption at 514 nm, the nonlinearity must be nonresonant. Hence we conclude that diacetylene monomer **1** is a promising third-order nonlinear optical material.

Discussion

On the basis of the experimental results obtained here, it appears that AM1 can be successful at modeling the properties of diacetylenes. The behavior of both compounds **1** and **2** is consistent with the AM1 calculations. Compound **1** is predicted to be unreactive for polymerization in the solid state, and such is indeed found to be the case. On the other hand, compound **2** is predicted to be very reactive for polymerization, and the experimental results appear to corroborate this prediction as well (it seems reasonable to assume that since this diacetylene polymerizes spontaneously in solution, it would also polymerize readily in the solid state). Because we are unable to isolate diacetylene **2** or its polymer, we cannot compare the nonlinear optical properties of the poly(diacetylenes) obtained from **1** and **2** and test the predictions based on the bandgaps computed using AM1.

The fact that diacetylene monomer **1** is liquid at room temperature is quite interesting, as is also the fact that it undercools readily. This behavior may be linked to the difficulty in polymerizing compound **1** in the solid state. It indicates that the monomer molecules only reluctantly pack into a crystal, which, in turn, suggests that the crystal structure may be somewhat strained sterically and, thus, is probably unfavorable for polymerization. Also, as mentioned earlier, it may be possible to polymerize diacetylene **1** in the liquid state, which might provide an interesting alternative to solid-state polymerization.

The discovery of good third-order nonlinear optical effects from the monomer **1** is very exciting. At present, the origin of these effects is still a mystery, especially considering the limited conjugation possible for this compound. The excellent phase conjugation exhibited by **1** in solution may be very useful for signal processing. A phase-conjugate mirror constructed using **1** could possibly be used to improve the signal-to-noise ratios of laser communication satellites in space. We are currently preparing thin polymer films containing compound **1** that can imitate the behavior in solution; such films would be more practical than liquid solutions for device fabrication.

Conclusions

It appears that computer modeling can be useful for predicting the chemical and optical properties of diacetylenes and their polymers. Such models could save labor in the laboratory by screening compounds which polymerize readily from ones which do not. The diacetylene derivatives of pyrrole studied here (particularly compound **1**) proved to be quite interesting and novel compounds. Future work in this area will concentrate on using AM2 (and other computer methods) to model additional poly(diacetylenes) which may have potentially useful chemical and optical properties, and on elucidating the nonlinear optical properties of other diacetylene monomers.

Experimental Section

Computations were performed using the AM1 method in version 5.04 of the MOPAC program, available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN (Program No. 455).[5] The supercomputer used was a CRAY X-MP/24, provided by the Alabama Supercomputer Network. A detailed treatment of these and other semiempirical molecular orbital calculations on poly(diacetylenes) will be published separately.[7] Unless otherwise specified, all reagents were purchased from Aldrich and used without further purification. ^{1}H-NMR spectra were run in d_6-acetone using an IBM Bruker 200-MHz Fourier transform spectrometer. Characterization experiments were carried out at Alabama A&M University under the direction of Dr. Hossan Abeledeyem.

Synthetic Methods. A. 3-Bromopropargyl Alcohol.[13] To a solution of 150 g of NaOH in 400 mL of water, cooled in an ice bath, is added slowly 25 mL of liquid bromine. To this solution is added 24 mL of propargyl alcohol, and the cooled mixture is stirred for 2–3 h. This mixture is then extracted with 500–600 mL of ethyl ether, in 75–100-mL portions. The ether is rotoevaporated, and the crude bromopropargyl alcohol is vacuum distilled at 50 °C/3–4 mmHg pressure (nitrogen atmosphere). Yield: 35–40 g (70%). ^{1}H-NMR: 4.22 ppm, s (CH_2).

B. *N*-Propargylpyrrole.[14] To 10 g of potassium metal in a 300-mL three-necked flask equipped with a condenser, an addition funnel, and a nitrogen inlet and surrounded by a water bath at room temperature is added a solution of 75 mL of pyrrole in 75 mL of anhydrous ethyl ether. The mixture is stirred rapidly as the potassium slowly reacts with the solution to form the potassium salt of pyrrole, which generally takes overnight to complete. Upon completion of the reaction, 100 mL of anhydrous ether is added, stirring is halted, and the suspension of the potassium pyrrole salt in ether is allowed to settle (about 15 min). The solution above the salt is then decanted off (keeping nitrogen flowing over the salt), and 10 mL of pyrrole and 35 g of an 80% by wt solution of propargyl bromide in toluene are added. A few pieces of ice are added to the water bath surrounding the mixture, and the mixture is then stirred for about 1 h. During this time the reaction between the potassium pyrrole salt and propargyl bromide begins slowly, but then becomes more vigorous (the mixture may begin to reflux). After the reaction has settled down, the water bath is removed and replaced by an oil bath, and the

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[18] He, K. X.; Abeledeyem, H.; Sekhar, P. C.; Venkateswarlu, P.; George, M. C. *Opt. Commun.* **1991**, *81* (12), 101.

[19] Marburger, J. H. *Prog. Quantum Electron.* **1975**, *4*, 35.

mixture is then heated for 2–3 h at 85–90 °C (oil bath temperature), the nitrogen flow being maintained. After the reaction is complete, the nitrogen flow is stopped, and 150 mL of water and 50 mL of ether are added to the reaction mixture. This mixture is then poured into a separatory funnel, the organic layer is separated and dried over anhydrous magnesium sulfate, and the ether is rotoevaporated off. The excess pyrrole and toluene are removed at 10 mmHg (bp 30–35 °C), and the *N*-propargylpyrrole is then distilled over at 45–55 °C/2–3 mmHg. Yield: 8–10 g (25–30%); this compound should be stored in a refrigerator under nitrogen and used within 1 or 2 weeks. ^{1}H-NMR: 6.79 ppm, t, 2 H (pyrrole ring); 6.08 ppm, t, 2 H (pyrrole ring); 4.78 ppm, d, 1 H (CH_2); 2.93 ppm, t, 1 H (acetylene CH).

C. Diacetylene 1.[11] This procedure was carried out in the dark the first time, but since it was found that the compound is not very light sensitive, this is not necessary. To a stirring solution of 0.20 g of cuprous chloride in 20 mL of 70% aqueous ethylamine and 15 mL of 95% ethanol in a three-necked flask equipped with an addition funnel and flushed with nitrogen is added 2.0 g of *N*-propargylpyrrole. Within 1 or 2 min the blue color of the solution should fade and a white precipitate will appear in the solution. To this solution is added dropwise (over 1–2 h) a solution of 3.0 g of bromopropargyl alcohol in 25 mL of 95% ethanol, a reaction temperature of about 35 °C being maintained. About 1 h after the addition is started, a tiny amount of hydroxylamine hydrochloride is added to the reaction mixture, changing the blue-green color of the mixture to brown. After about 2 h the reaction is stopped, and all of the solvent is removed under vacuum until a viscous residue is left. To this is added 75 mL of benzene, the mixture is stirred for 5 min, about 2–3 g of anhydrous magnesium sulfate is added, the mixture is stirred for 5 min more, and the solid is then filtered off. The brown solution containing the crude diacetylene is then run down a silica gel column to purify the diacetylene. About 2–3 g of silica gel packed in a 1 cm diameter column is used to purify a 25-mL aliquot of the diacetylene solution. The silica gel is placed in the column and washed with benzene, and 25 mL of the diacetylene solution is loaded onto the column. The first 20 mL of eluent is discarded (this contains a small amount of the symmetrical diacetylene, compound **16** in Table I), and the column is then eluted with an additional 100 mL of benzene. The resulting light yellow solution contains the purified diacetylene, which is then isolated by removing the benzene under vacuum. The remaining portions of the diacetylene solution are purified in the same way, using fresh silica gel for each 25-mL aliquot. Yield: 1.0 g (30%). ^{1}H-NMR: 6.78 ppm, t, 2 H (pyrrole ring); 6.08 ppm, t, 2 H (pyrrole ring); 4.92 ppm, s, 2 H (CH_2 next to pyrrole ring); 4.48 ppm, t, 1 H (OH); 4.28 ppm, d, 2 H (CH_2 next to OH). Occasionally these latter two peaks appear as singlets.

D. *N*-(α,β-Dichlorovinyl)pyrrole.[16] From 10 g of potassium metal the pyrrole salt is prepared as described above. In this case, after the solution is decanted off from the potassium pyrrole salt, 100 mL of trichloroethylene is added, and the mixture is stirred under reflux overnight (keeping nitrogen flushing through the system). The brown-black mixture is then filtered, and the filtrate is rotoevaporated to remove ether and excess trichloroethylene. Excess pyrrole is distilled off at 30–35 °C/10 mmHg, and the *N*-(α,β-dichlorovinyl)pyrrole is then distilled over at 50–55 °C/2–3 mmHg. Yield: 20 g (50%). ^{1}H-NMR: 7.04 ppm, t, 2 H (pyrrole ring); 6.65 ppm, s, 1 H (vinyl CH); 6.27 ppm, t, 2 H (pyrrole ring).

E. *N*-Ethynylpyrrole.[17] To 100 mL of stirring 1.4 M methyllithium in ether in a round-bottom flask, equipped with an addition funnel, a nitrogen inlet, and surrounded by a bath at −10 °C (ethylene glycol slush), is added dropwise 10 g of *N*-(α,β-dichlorovinyl)pyrrole in 10 mL of ether over a period of about $^1/_2$ h. After the addition is complete, the mixture is allowed to warm to room temperature for about 1 h and then cooled back down to −10 °C, and 25 mL of saturated aqueous NaCl is added dropwise over a few minutes. The mixture is then allowed to warm to room temperature, the solution is decanted from the solid remaining in the bottom of the flask, and 100 mL of water is added to dissolve the solid. This solution is extracted with two 50-mL portions of ether, and these extracts are combined with the original solution decanted from the reaction mixture. The combined extracts are washed with 50 mL of water and dried over anhydrous magnesium sulfate, and the ether is then rotoevaporated off, leaving crude *N*-ethynylpyrrole. When all traces of ether have been removed, the compound is purified by means of flash distillation at 30 °C/1 mmHg pressure using a chloroform slush bath condenser (−60 °C). Yield: 5–6 g (90%); *N*-ethynylpyrrole should be stored refrigerated under nitrogen and used within a week. ^{1}H-NMR: 7.00 ppm, t, 2 H (pyrrole ring); 6.20 ppm, t, 2 H (pyrrole ring); 3.46 ppm, s, 1 H (acetylene CH).

F. Diacetylene 2.[11] This reaction was carried out in the dark in the same manner as that for compound **1**, using *N*-ethynylpyrrole instead of *N*-propargylpyrrole. The NMR spectrum of the crude reaction mixture indicates the presence of **2** and/or its polymer, but extraction with benzene yields a mixture of products, including a very small amount of the monomer **2** (not enough to isolate). Thus we suspect that diacetylene **2** undergoes spontaneous polymerization (as well as other side reactions) upon formation in the reaction. ^{1}H-NMR (tentative assignments based on comparison with the NMR spectrum of **1**): 6.77 ppm, s (br), 2 H (pyrrole ring); 6.05 ppm, s (br), 2 H (pyrrole ring); 4.28 ppm, s, 2 H (CH_2 next to OH).

Vapor Growth and Polymerization of Compound 1. About 300–500 mg of the liquid monomer **1** is placed in the bottom of the vapor deposition apparatus (the volume inside this apparatus is about 75 mL). Thin crystalline films of the monomer are grown onto circular quartz disks (about 1.5–2.0-cm diameter and 3-mm thickness) using a source temperature of 30–32 °C and a condenser temperature of −20 °C at a pressure of 20 μmHg (see Figure 2). Typically, about 24 h is required to grow a film.

Once a monomer film has been grown, the vapor growth apparatus is filled with nitrogen, the film is left on the condenser (maintained at −20 °C), and the bottom portion of the apparatus containing the source material is removed and replaced with a quartz bottom (the source material can be saved and used again to grow more films). The vapor growth apparatus is then refilled with nitrogen, and the film is polymerized (still at −20 °C) using a 100-W 365-nm UV lamp (the lamp is placed about 9–10 cm from the film). The polymerization is complete after 3 days; the resulting yellow-brown poly(diacetylene) film can then be warmed to room temperature and is ready for characterization.

Characterization of Compound 1. When the poly(diacetylene) films obtained from compound **1** are subjected to the 514-nm beam of an argon ion laser, there is no light transmitted through the films (even with very thin films). When a frequency-doubled Nd:YAG laser is used (532 nm), the films bubble and flake off of the quartz disks. Thus we conclude that the optical and mechanical properties of this poly(diacetylene) probably preclude exploitation of any useful third-order nonlinear optical properties it may possess.

To characterize the monomer **1**, a sample is purified by means of vapor deposition and a 30 mg/mL solution is prepared in acetone. The nonlinear (intensity-dependent) refractive index for this solution is determined by the technique of self-trapping.[19] This method consists of passing the 514-nm beam of an argon ion laser through the solution (in a 1-cm quartz cell) and projecting the beam onto a screen (placed about 1 m from the cell). The laser power is varied until the minimum power (the critical power, P_c) required to observe multiple diffraction rings on the screen (as a result of self-phase modulation) is found; from this the intensity-dependent refractive index, n_2, is determined as 3.3×10^{-6} esu using eq 1:

$$n_2 = \frac{1.86c\lambda}{16\pi^2 P_c} \tag{1}$$

where c is the speed of light in vacuum and λ is the wavelength of the laser light. Assuming a value of $n_0 = 1.36$ for pure acetone as the linear (intensity-independent) refractive index of the solution, the $\chi^{(3)}$ value for this solution is calculated as 4.8×10^{-7} esu using eq 2.

$$\chi^{(3)} = \frac{n_0}{3\pi} n_2 \tag{2}$$

This measurement was repeated twice to insure that a spurious result was not being observed; the same value was obtained each time. The UV–visible absorption spectrum of diacetylene monomer **1** was determined in acetone. The absorption maximum, λ_{max}, was found to be around 330 nm, and there was no absorption at 514 nm (or 532 nm); hence we conclude that the third-order nonlinearity of this compound is nonresonant. The $\chi^{(3)}$ value for phase conjugation (four-wave mixing) at 532 nm is currently being determined.

Registry No. 1, 139565-84-7; **1** (homopolymer), 139566-05-5; **2**, 139565-85-8; **3**, 460-12-8; **4**, 6089-44-7; **5**, 51104-87-1; **6**, 2809-69-0; **7**, 4911-55-1; **8**, 139565-86-9; **9**, 3031-68-3; **10**, 15808-23-8; **11**, 139565-87-0; **12**, 14400-73-8; **13**, 886-66-8; **14**, 139565-88-1; **15**, 139565-89-2; **16**, 139565-90-5; **17**, 113274-97-8; **18**, 139565-91-6; **19**, 113487-60-8; $Br(C{\equiv}C)_2CH_2OH$, 54542-21-1; $HC{\equiv}CCH_2OH$, 107-19-7; $HC{\equiv}CCH_2Br$, 106-96-7; $ClCH{=}CCl_2$, 79-01-6; pyrrole potassium salt, 16199-06-7; *N*-propargylpyrrole, 19016-98-9; *N*-(dichlorovinyl)pyrrole, 139565-92-7; *N*-ethynylpyrrole, 139565-93-8.