OPEN ACCESS

GAVIN PUBLISHERS

Current Research in
Bioorganic & Organic Chemistry

Research Article

Nwokogu GC and Simpson S. Curr Res Bioorg Org Chem 2: 119.
DOI: 10.29011/2639-4685.100019

Effect of Remote Polyene Bridge Methyl Substituent on Physical Properties of Dipolar Chromophores with Conformationally and Configurationally Locked Polyene Bridge

Godson C. Nwokogu*, Samuel Simpson

Department of Chemistry and Biochemistry, Hampton University, Hampton, VA 23668, USA

***Corresponding author:** Godson C. Nwokogu, Department of Chemistry and Biochemistry, Hampton University, Hampton, VA 23668, USA. Tel: +17577275276; Email: godson.nwokogu@hamptonu.edu

Citation: Nwokogu GC, Simpson S (2019) Effect of Remote Polyene Bridge Methyl Substituent On Physical Properties of Dipolar Chromophores with Conformationally and Configurationally Locked Polyene Bridge. Curr Res Bioorg Org Chem 2: 119. DOI: 10.29011/2639-4685.100019

Received Date: 28 January, 2019; **Accepted Date:** 11 February, 2019; **Published Date:** 19 February, 2019

Abstract

The effect of a C-2 substituent on the success of Knoevenagel condensation of the cycloalkenone moiety, which is usually the final step in the multi-step synthesis of conformationally and configurationally locked polyene bridged Donor - π - Acceptor chromophores, has been investigated. In addition, the possibility of a two-pot synthesis of polyene bridges with more than two annulated cyclohexenyl rings and the effect of a polyene bridge methyl substituent on the planarity of the chromophore have been investigated. The results of these studies show that a C-2 on the terminal cycloalkenone of the polyenone must not be substituted for successful Knoevenagel condensation in the modular synthesis of Donor-π -Acceptor dipolar chromophores. It is also demonstrated that three new rings can be annulated in a two-pot reaction sequence. A significant blue shift in λ_{max} of prepared rigid polyene bridge chromophores indicates that a remote methyl substituent on the polyene bridge has a dramatic effect on the planarity of the chromophore.

Keywords

Blue Shift; Chromophore; Donor-π-Acceptor; Knoevenagel Condensation; Poly-Michael Addition; Polyene Bridge; Poly-Aldol; Remote Methyl Substituent.

Introduction

The electro-optic applications of polymeric devices are based on the second order Non-Linear Optical (NLO) properties of low molar mass dipolar chromophores incorporated into the polymeric material either by physical mixing or through covalent linkage. These dipolar small molecules often have a donor-π polyene bridge-acceptor (D - π - A) motif. Unlike inorganic analogs, the NLO- and other physical properties of organic dipolar molecules can be optimized synthetically. Synthesis has been applied to improve properties of organic dipolar chromophores such as the thermal stability at processing temperatures above 200°C [1], the length of the polyene bridge that connects the electron-donating and electron-withdrawing moieties [2] and the strength of the electron-donating and electron-withdrawing groups [3]. Loss of asymmetry during normal assembly of non-linear optical organic polymers was overcome by electric poling of molten NLO-endowed polymer and allowing to solidify under poling electrical voltage [4].

Synthesis has demonstrated that incorporating the polyene bridge into annulated cycloalkenyl rings leads to improvements in various characteristics of the dipolar chromophores such as: (a) electrostatic stacking [4c] (b) thermal stability which allows electrical poling and device fabrication, [4b, c, 5] (c) transparency of polymeric films endowed with dipolar chromophores, and

(d) chemical stability of the polyene bridge to conjugate addition [4c, 6]. Shu et al compared the decomposition temperatures of ring-rigidified polyene bridged against analogous open chain polyene bridged chromophores and found dramatic improvement in the thermal stability of the rigidified polyene bridged when compared with identical open chain polyene bridged analogs [6-8].
Another intriguing result of the work reported by Shu et al comes from the analysis of solid-state structures of the fused cyclic and the open chain polyene bridge chromophores by X-ray crystallography. Their analyses determined that the two types of polyene bridged compounds have nearly planar structure, with the electron-donating phenyl and the electron-withdrawing dicyano groups showing a 4° twist angle for the annulated bridge and 11° twist angle for the open chain analog respectively [6]. These results show that the chromophore with annulated polyene bridge is closer to planar than the open chain bridge analog. A closer to planar conjugated dipolar molecule implies better electron delocalization of the π-system of the push-pull molecule. The minor effect of enclosing the polyene bridge into annulated rings on planarity was consistent with the small (10 - 12 nm) blue shift in the λ_{max} values determined for the rigidified bridge chromophores relative to their open chain analogs with same number of alternating double/single bonds [6]. To our knowledge, there has been no reported inquiry into the effect of substitution on the annulated polyene bridge on the planarity and electron delocalization in such dipolar chromophores. There has been no study on how a significant shift in planarity of the annulated polyene bridge would affect transparency and other properties as the bridge is elongated because a shorter synthetic scheme for such chromophores has not been investigated till now.

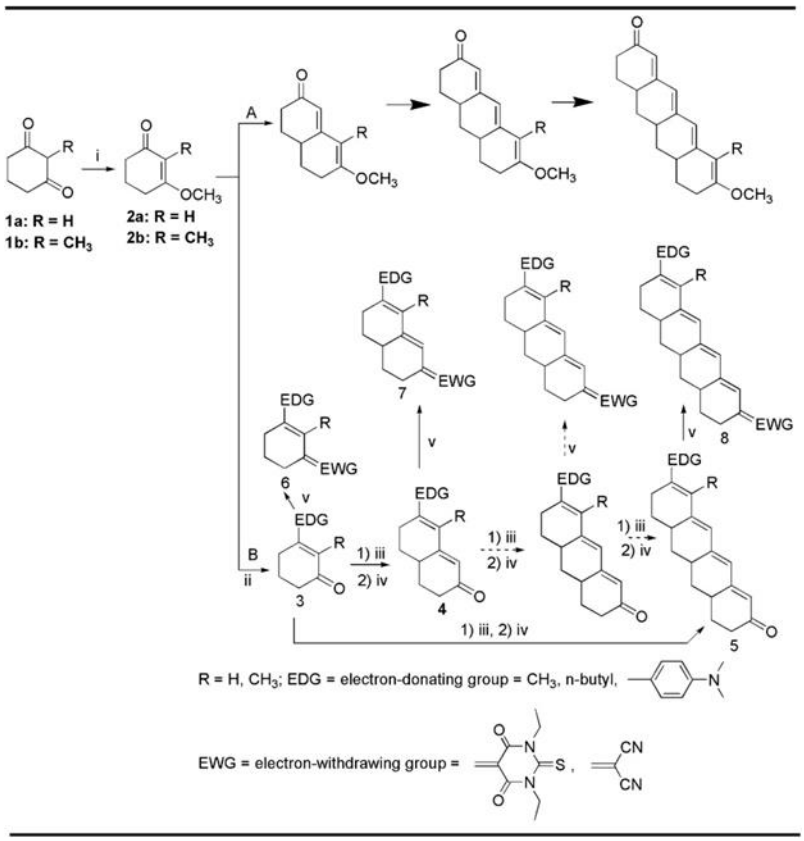
The most rigidified polyene bridge chromophores should have all the polyene bridge C=C bonds incorporated into annulated cyclohexenyl rings except the double bond connecting the bridge to the electron-withdrawing group. To achieve this maximum rigidization, the reported synthetic scheme usually starts with a1, 3-cyclohexanedione. Shu et al. [6] have prepared bicyclic and tricyclic polyenones starting with 5, 5-dimethyl-1,3-cyclohexanedione. In the reported scheme, each additional ring annulation was achieved by repetitive two-step schemes each starting with the generation of the kinetic enolate of the cyclohexenone, followed by Michael addition to methyl vinyl ketone. The resulting Michael adduct was isolated and then subjected to intra-molecular aldol condensation under basic condition. We considered that poly-Robinson annulation in a two-pot reaction sequence involving poly-Michael addition followed by a poly-intra-molecular aldol condensation would dramatically reduce the number of reaction steps for the preparation of elongated annulated polyene bridge systems.

All currently reported annulated polyenones that have successfully undergone Knoevenagel condensation in the final step of the modular synthesis of annulated chromophores have involved polycyclic polyenones with no substitution on the sp^2-carbon that is α to the carbonyl carbon [4-8]. A literature search also showed that reported cyclohexenone analogs that have so far successfully undergone Knoevenagel condensation have no substituent at the C-2 carbon of the cyclohexenone moiety [9]. Since the low reactivity of enones has already been acknowledged as a bottleneck in the successful conclusion of any scheme for the modular assembly of push-pull chromophores [4b], it would be advantageous to establish the effect of a substituent on the C-2 carbon of cyclohexenones on the ability to effect their Knoevenagel condensation. Certainty in the success of the Knoevenagel condensation is especially necessary before embarking on the long synthesis of any elongated annulated polyenone that would require 2(n-1) reaction steps to create the (n-1) annulated rings of the rigidified polyene bridge, where n is the number of six-membered rings of the polyene bridge. In this report, we present results from our examination of the following questions related to the optimization of the synthesis and properties of D− π − A chromophores with ring-locked polyene bridges: (a) what is the effect of a C-2 substituent on the success of the Knoevenagel condensation used to connect cyclohexenones and annulated poly-cyclohexenones to the electron withdrawing moiety of the chromophore in the last step of a modular synthesis? (b) will poly-annulation be possible in one sequence of one-pot multiple Michael addition reactions, followed by one-pot multiple intra-molecular aldol condensation reactions instead of the current repetitive sequence that annulates each additional ring in two reactions? and (c) how will a remote substituent on the annulated polyene bridge affect planarity of the chromophore and subsequently, its properties such as melting point (mp), thermal and chemical stability, λ_{max} and transparency?

Results and Discussion

Two pathways for the modular synthesis of completely annulated polyene bridges are given in Scheme 1. Pathway A has been used by Shu et al. [6] to prepare bicyclic and tricyclic annulated polyene bridged chromophores. In this pathway, the polyenone bridge

Scheme 1: Two Routes for the Modular Synthesis of Conformationally and Configurationally Locked or Rigidified Push-Pull Polyene Chromophores.[a]



[a]Reagents: (i) $HC(OCH_3)_3$, Amberlite IR-120(plus), abs. MeOH; (ii) RLI or RMgBr; (iii) LDA, MVK, -78°C; (iv) *t*-BuOK, *t*-BuOH/ THF, 25°C; (v) malononitrile or thiobarbituric acid, CCl_4, azeotropic distillation.

is constructed first as an elongated vinylogous ester. The Electron Donating Group (EDG) is attached to the carbonyl carbon of the ether-polyenone by nucleophilic addition. Unmasking of the ether ring carbon as a carbonyl group, followed by the attachment of the Electron Withdrawing Group (EWG) to the polyenone by Knoevenagel condensation completes the synthesis of the push-pull chromophore. We have developed pathway B because the early attachment of a strong electron donating group is expected to increase the donor character of the kinetic enolate of the cyclohexenone in the subsequent Michael addition. It should be noted that the locations of the EDG and EWG in pathway A are opposite in pathway B in terms of the starting and ending cyclohexene rings of the annulated polyene bridge.

Synthesis of:

3-Substituted Cyclohexenones with and Without C-2 Methyl Substituents:

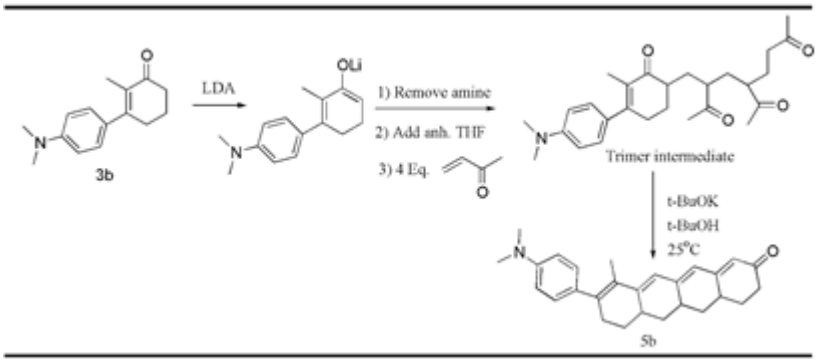
The vinylogous esters **2a** (R_1 = H) [10] and **2b** (R_1 = CH_3) [10] were prepared in high yields from 1,3-cyclohexanedione **1a** and 2-methyl-1,3-cyclohexanedione **1b** respectively by stirring at room temperature with trimethyl orthoformate in anhydrous methanol in the presence of Amberlite IR-120(plus) as catalyst [11b]. Treatment of the vinylogous esters with n-butyllithium or either the Grignard or the lithium derivative of p-N, N-dimethylaminophenyl bromide produced the 3-n-butyl and the 3-(p-N, N-dimethylaminophenyl) substituted cyclohexenones **3a** (R = H; EDG = n-butyl) [12], 3**b** (R = H; EDG = p-N, N-dimethylaminophenyl), **3c** (R = CH_3, EDG = p-N, N-dimethylaminophenyl) respectively in good yields after acid work-up. In our hands, the organolithium reagents gave better reactions than their Grignard analogs. The 3-alkylsubstituted cycloalkenones were candidates for the investigation of the effect of C-2 substituent on the success of Knoevenagel condensation of cycloalkenones only, whereas the enones with the electron-donating p-N, N-dimethylaminophenyl substituent were also candidate compounds for the investigation of the effect of a polyene bridge methyl substituent on the properties of rigidified bridge push-pull chromophores.

Annulated Polycyclohexenones with and Without a Methyl Substituent on the Polyene Bridge:

The bicyclic fused ring polyenones 4**a** (R, = H, EDG = p-N, N-dimethylaminophenyl) and **4b** (R = CH_3; EDG = p-N, N-dimethylaminophenyl) were prepared by Michael addition of methyl vinyl ketone to the kinetic enolates of 3-substituted cyclohexenones **3a** and **3b** followed by intra-molecular aldol condensation of the respective products using *t*-BuOK in a mixture of *t*-BuOH and THF at room temperature. In contrast to the way this reaction has been run by others [6,8] we have used the procedure reported by Reusch and co-workers [13] which requires removal of the amine formed in the enolate generation step before the conjugate addition reaction step. This procedure was proposed to eliminate reaction of the amine with the Michael acceptor which would decrease the yield of the desired product.

The tetracyclic polyenone **5b** (R = CH_3; EDG = p-N, N-dimethylaminophenyl) was obtained in low yield as a red solid according to Scheme 2 when four equivalents of methyl vinyl ketone were used in the Michael addition step.

Scheme 2: Abbreviated Triple Annulation



The material isolated after the Michael addition was a viscuous oil which we assumed to be the trimer intermediate in Scheme 2. The trimer was isolated but not characterized before being subjected to a one-pot, multiple annulations to give the tetracyclic polyenone **5b** whose structure was confirmed by standard methods.

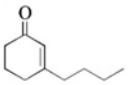
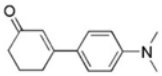
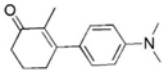
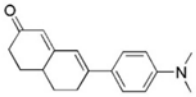
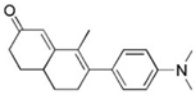
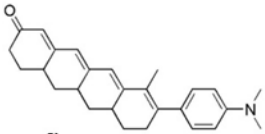
A tricyclic annulated polyene bridge is the longest that has been reported before this [6]. The tricycle was assembled in four steps involving two repetitive sequences of conjugate addition of methyl vinyl ketone to the kinetic enolate of a cyclohexenone followed by intra-molecular aldol condensation of the Michael adduct. The two-pot synthesis of a tetracyclic annulated polyene bridge illustrated in Scheme 2 would have otherwise taken six steps by the usual method. The result reported here suggests that multiple annulated rings can be prepared in a highly abbreviated manner. It also raises the possibility that the number of newly annulated rings can be controlled based on the amount of Michael acceptor and reaction condition used.

Effect of a C-2 Methyl Substituent on the Knoevenagel Condensation of Cyclohexenones:

The Knoevenagel condensation [9c,14] is a useful reaction for creating a C=C bond between the carbonyl carbon of an aldehyde or ketone and the methylene carbon of activated methylene compounds. The reaction works best with aldehydes but has been found to be less successful with ketones. Similar trend is observed with α,β-unsaturated aldehydes and ketones. The extension of this condensation to polyenic aldehydes [5a, 6,8] and cyclic polyenic ketones [4b, 5a, 6,7] has become an important last step in the modular synthesis of push-pull chromophores. The modular synthetic scheme for push-pull molecules by pathway B (Scheme 1) consists of three modules: 1) connecting an EDG to a cyclohexenone by nucleophilic addition, 2) elongating the EDG bearing cyclohexenone into annulated polyenone bridge by series of Michael addition followed by intra-molecular aldol condensation and 3) attaching an EWG to the polyenone by Knoevenagel condensation. The reported examples of successful Knoevenagel condensation with cycloalkenones so far have used mostly 3-alkylcycloalkenones [9] where the C-3 substitution was probably intended to block conjugate addition of the nucleophile generated from the activated methylene compound. These cycloalkenones possess no substituent on the vinyl C-2-carbon and there is no report on the effect of C-2 substituent on the feasibility of Knoevenagel condensation with cycloalkenones.

In the synthetic optimization of the Non-Linear Optical (NLO) properties of push-pull chromophores, it is of interest to identify the scope of Knoevenagel condensation of cyclohexenone and its derivatives which can be the last step in a multistep, modular assembly of push-pull chromophores. We therefore undertook a study of the effect of C-2 substitution on the success or failure of the Knoevenagel condensation of cycloalkenones. To investigate this scope, we prepared various cyclohexenone derivatives as well as annulated cyclic polyenones (Table 1) with and without C-2 methyl substituent. These cyclohexenones were then subjected to

Table1: Structures, Yields and Melting Points of Cyclohexenones Prepared for This Study

Cyclohexenones	Yield (%)	Melting Point (°C)
 **3a**	89	Liquid
 **3b**	78	133.7
 **3c**	93	97.6
 **4a**	36	206.1
 **4b**	95	175.3
 **5b**	11	300.5

Knoevenagel condensation under various reaction conditions to determine how C-2 substitution might affect the success of the last step in the multi-step modular synthesis of a poly-annulated polyene bridge chromophores such as **7**and **8** (Scheme.1). The result of this investigation will inform on the structural requirement for the efficient introduction of the electron-withdrawing group in the final step of the modular synthesis of push-pull chromophores with conformationally [6-8] and configurationally [5a, 6] locked polyene bridges. Incorporation of the polyene bridge into annulated rings imparts rigidity to it and locks it in the *s-trans* conformation and the (E) configuration.

The two activated methylene compounds used in our study are 2- thiobarbituric acid, C and malononitrile D (Figure 1), which introduce the corresponding electron-withdrawing group after condensation with the cyclohexenones.

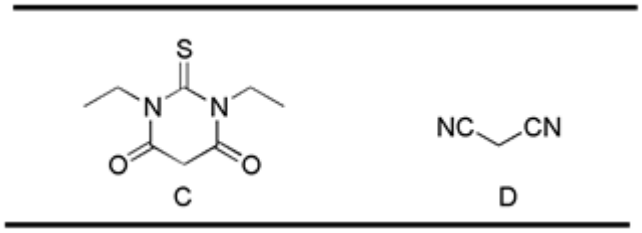


Figure 1. Synthetic Equivalents of the Electron-withdrawing Group Synthons

2-Methylcyclohexenone **3b** (Table 2) failed to condense with 1, 3-diethyl-2-thiobarbituric acid C in alcohols, benzene or methylene chloride. Use of various amine/glacial acetic acid combinations or simple amine salt catalysts at temperatures ranging from the boiling point of the reaction solvent up to 160°C did not lead to condensation. No conjugate addition product was isolated from the reaction mixture after each attempted reaction. Even in the case of 2-methylcyclopentenone **10**, [15] which does not possess a C-3 substituent, neither Knoevenagel condensation nor conjugate addition products were identified from the attempted condensation reaction (Table 2). In these experiments, only unreacted cycloalkenone was recovered from the reaction mixture.

On the other hand, cyclohexenones **3a** (R = H; EDG = n-butyl), **4a** (R = H; EDG = p-N, N-dimethylaminophenyl), **4b** (R CH_3; EDG = p-N, N-dimethylaminophenyl) and **5b** (R = CH_3; EDG = p-N, N-dimethylaminophenyl) which do not possess C_2-substituent, reacted quite well and easily in carbon tetrachloride, chloroform or the ionic liquid, 1-methyl-3-octylimidazolium tetra fluoroborate, to produce the expected condensation products. The chromophores were less stable in chloroform and the ionic liquid. Isolation of the product from the ionic liquid also required a lot of solvent for product extraction. Most Knoevenagel condensation reactions were therefore run in CCl_4. The cyclohexenone **3a** gave a quantitative yield of condensation product **6a** with 1, 3-N, N-diethyl-2-thiobarbituric acid (Equation 1) and a fair yield of **6b** with malononitrile (Table 2). No adducts were formed when the cyclohexenone **3b** was reacted with either thiobarbituric acid or malononitrile. Table 2 summarizes the results of the

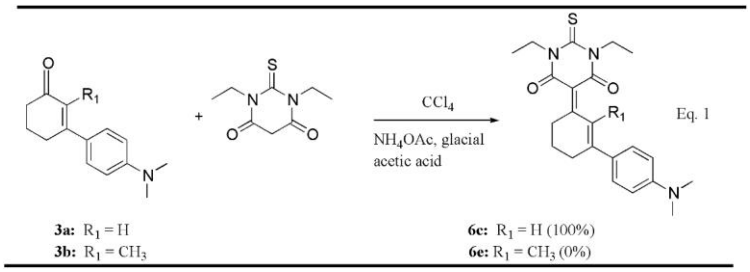
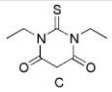
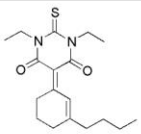
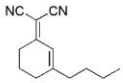
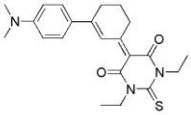
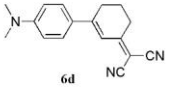
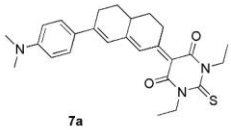
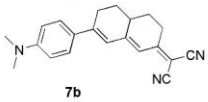


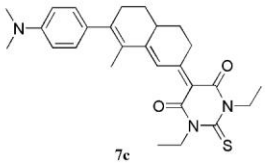
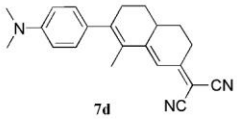
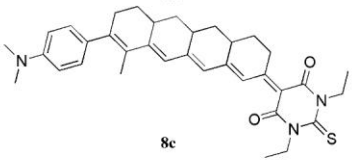
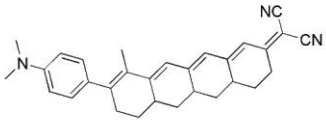
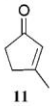
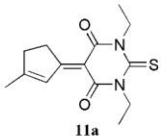
Table 2: Knoevenagel Condensation of Cycloalkenones with Activated Methylene Compounds.

Cyclohexenone	Methylene Compound	Adduct	Yield(%)
3a	 C	 **6a**	79
3a	D	 **6b**	63
3b	C	 **6c**	100
3b	D	 **6d**	53
3c	C or D	No Reaction	0
4a	C	 **7a**	100
4a	D	 **7b**	76

attempted Knoevenagel condensation of the cycloalkenone with the two methylene compounds used in this study. The cyclopentenones **10** and **11** in Table 2 illustrate that the observed trend is not limited to cyclohexenones. The progress and completion of the Knoevenagel condensation of enones and polyenones with the activated methylene compounds can be monitored using ^{1}H NMR spectroscopy due to the significant chemical shift difference between the C-2 proton of the enone and its electron withdrawing condensation adduct. Attachment of the electron withdrawing group moves the chemical shift of the C-2 proton of the cyclohexenone moiety from between 6.00 - 7 ppm to up to 9.00 ppm for the thiobarbituric acid adduct and up to 7.20 ppm for the malononitrile adduct (Figure 2). Condensation reactions can therefore be run until proton NMR spectrum shows either total disappearance or just trace of the enone C-2 proton in the crude reaction mixture, especially when CCl_4 is used as reaction solvent.

These Knoevenagel condensation results lead to the conclusion that the terminal cyclohexenone ring of an annulated polyenone must not be substituted at C-2 for successful Knoevenagel condensation under the reaction conditions used in this study. Remote substituents on the fused ring polyene do not appear to hamper the condensation reaction as illustrated by the successful condensation of polyenones **4b** and **5b**. Thus, assembly of the annulated polyenone bridge must be terminated through a final Robinson annulation using methyl vinyl ketone as the Michael acceptor in order to form the desired terminal C-2 unsubstituted cyclohexenone ring.

Table 2 Cont'd:

Cyclohexenone	Methylene Compound	Adduct	Yield(%)
4b	C	 **7c**	100
4b	D	 **7d**	17
5b	C	 **8c**	67
5b	D	 **8d**	29
10	C or D	No Reaction	0
 **11**	C	 **11a**	80
11	D	**11b**	71

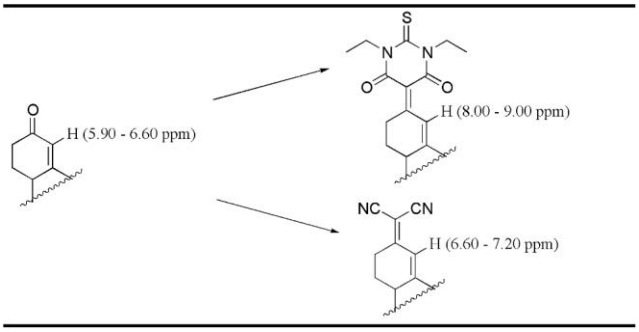


Figure 2: Effect of electron-withdrawing group on the chemical shift of C-2 proton of adducts.

Effect of a Polyene Bridge Vinyl Methyl Substituent on Planarity and Some Physical Properties of the Push-Pull Chromophores:

Shu et al. [6,8] studied the planarity of unsubstituted open chain and annulated polyene bridged push-pull chromophores by X-ray crystallography and concluded that enclosing the polyene bridge into fused cyclohexenyl rings did not significant decrease the planarity and effective electron delocalization of the π−bridge. This conclusion is in agreement with both the about 10 nm difference in the λ_{max} and almost identical Bond Length Alternation (BLA) [16] values determined for open chain and annulated/rigid structures that have the same number of double bonds in the polyene bridge. In this study, we examined the effect of a polyene bridge methyl substituent on the planarity of annulated polyene bridge D-π−A chromophores based on λ_{max} values. We found that the blue shift in the λ_{max} values of annulated bridges that differ only in the presence of a methyl substituent on the cyclohexenyl ring bearing the electron-donating aromatic ring was 71 nm for the thiobarbituric acid derivatives **7a** (R = H; EDG = p-N,N-dimethylaminophenyl; EWG = thiobarbituric acid) versus **7c** (R= CH_3; EDG = p-N,Ndimethylaminophenyl; EWG = thiobarbituric acid) and 45 nm for the malononitrile analogs **7b** ((R = H; EDG = p-N,N-dimethylaminophenyl; EWG = malononitrile moiety) versus **7d** (R = CH_3; EDG = p-N,N-dimethylaminophenyl; EWG = malononitrile moiety) (Table 3). Based on the λ_{max} values reported by Shu for the malononitrile adducts of the bicyclic and tricyclic chromophores, we estimated that the unsubstituted tetracyclic analog **8a** ((R = H; EDG = p-N, N-dimethylaminophenyl; EWG = malononitrile moiety), which has not yet been prepared, will have a λ_{max} of ~ 540 nm. When this estimated value is compared with our measured λ_{max} value for **8d** (R = CH_3; EDG = p-N, N- dimethylaminophenyl; EWG = malononitrile moiety) of 496 nm, the methyl substituent is estimated to induce a blue shift of ~ 44 nm which is similar to the observed blue shift for our prepared bicyclic analogs. These significant blue shifts in the absorption maxima of methyl-substituted annulated polyene bridges lead to the conclusion that a remote (up to four rings away from the electron-withdrawing group) methyl substituent on the annulated polyene bridge significantly reduces planarity and electron delocalization in the polyene bridge.

There are also trends observed in the thermal properties of bridge-substituted vs bridge-unsubstituted rigidified chromophores that seem to depend on both the number of annulated rings and the nature of the electron-withdrawing moiety. Whereas the melting point increases as the number of rings increases for unsubstituted rigidified bridges as demonstrated by Shu et al [6], we found that melting point decreases immensely as the number of rings increases when a remote methyl substituent is present. For example, in the bridge-unsubstituted polyene bridges, mp increases from 204.5°C for the monocyclic adduct **6d** (R = H; EDG = p-N, N-dimethylaminophenyl; EWG = malononitrile moiety) to 235.7°C for the bicyclic adduct **7b** (R = H; EDG = p-N, N-dimethylaminophenyl; EWG = malononitrile moiety) respectively. But the mp of the bicyclic methyl-substituted analog **7d** is much

Table3: Some Physical Properties of Prepared Dipolar Chromophores.

Chromophore	Melting Point(°C)	λ_{max} (nm)	$\varepsilon/10^4(m^{-1}\ cm^{-1})$
6a	68	376	3.93
6b	Liquid	307	2.09
6c	226	551	4.58
6d	205	486	4.19
7a	262	572	3.64
7b	236	499	4.58
7c	185	501	2.1
7d	183	454	2.26
8c	262	574	5.24
8d	263	496	5.54
11a	148	366	4.68
11b	89	301	2.55

lower at 183°C than the monocyclic chromophore. For the thiobarbituric acid chromophores, the same trend was observed. The mp values are 225.8^{o}C for the unsubstituted monocyclic **6c**, 262.3^{o}C for the unsubstituted bicyclic **7a** but 184.7^{o}C for the methyl-substituted bicyclic chromophore **7c** respectively. One factor which may contribute to this observation may be the reduced planarity of the methyl substituted analogs which would result in less compact packing of molecules in the solid state. It was also noted that even though the thiobarbituric acid adducts of rigidified chromophores usually have significantly higher melting points than their malononitrile analogs for the unsubstituted bridge chromophores (~ 20° or more between **6c** vs **6d**; **7a** vs **7b**), the melting points of methyl-substituted thiobarbituric acid and malononitrile adduct chromophores with the same polycyclic bridge length differ by less than 2°C (see the mp of **7c** vs **7d** and **8c** vs **8d** in Table 3).

Conclusion

We have examined the effect of a C-2 substituent on the success of Knoevenagel condensation of cycloalkenone moiety in the final step of the multi-step synthesis of conformationally and configurationally locked polyene bridged donor – π – acceptor chromophores. In addition, the possibility of a two-pot synthesis of polyene bridges with more than two annulated rings and the effect of a mdethyl substituent on the polyene bridge on the planarity of the chromophore have also been investigated. The results of the studies reported here show that the C-2 on the terminal cycloalkenone of the polyenone must not be substituted for successful, final step, Knoevenagel condensation to complete the synthesis of the dipolar chromophores. We also demonstrated that three new rings can be annulated in a highly abbreviated two-pot reaction sequence. Measurements of the λ_{max} of prepared rigid polyene bridge chromophores indicate that a remote methyl substituent on the polyene bridge has a dramatic effect on the planarity of the chromophore bridge. This conclusion is based on the observed significant blue shifts in λ_{max}. The results of the three related studies reported herein represent important contributions to the knowledge base for the synthetic optimization of the properties of chromophoric organic materials. Monomers and polymers endowed with such optimized properties are important for the development of improved fabrication components for materials science and technology.

Experimental Section

General methods: Reagents were purchased from Aldrich Chemical Company of Milwaukee, Wisconsin, U.S.A. and used as received. Tetrahydrofuran (THF) and diethyl ether were dried by distillation over sodium benzophenone ketyl. Ionic liquid, 1-methyl-3-octylimidazolium tetrafluoroborate was purchased from Fluka. ^{1}H and ^{13}C spectra were recorded on JEOL ECS-400 NMR spectrometer using $CDCl_3$ containing 0.03% of tetramethylsilane (TMS) as internal reference. EM Science silica gel 60 (70 -230 mesh ASTM) or EM Science neutral alumina (70-230 mesh ASTM, Brockman Activity III) was used for chromatographic separations. UV-Vis absorption spectra were recorded on a Beckman DU-600 or Varian Associates Cary 50-BIO UV-Vis spectrophotometer in spectrophotometric grade CH_2Cl_2 or $CHCl_3$. Nominal mass spectra were run on a VG-7070 E-HF spectrometer and exact mass spectra were run on an Agilent TOF 6220 spectrometer. Melting points were determined on a TA Instruments DSC 2920 Modulated DSC at a heating rate of 10°C per minute. Elementary analyses were performed by Galbraith Laboratories Inc. of Knoxville, TN, U.S.A.

3-Methoxy-2-cyclohexen 1-one, **2a**[10]**:**

21.57 g of Amberlite IR-120(plus) was stirred for 24 h in absolute methanol. After the methanol was decanted from the Amberlite, it was replaced with 160 mL of fresh absolute methanol. Into the reaction flask were then added 62.33 g (556.52 mmol) of 1,3-cyclohexanedione and 80 mL of anh. trimethyl orthoformate. The mixture was stirred for 24 h at room temperature under nitrogen during which time a dark brown suspension was formed. The solution was decanted from the Amberlite and excess trimethyl orthoformate and methanol were distilled off under vacuum on an oil bath. The residual liquid from the distillation was extracted with hexane until a dark gummy residue was left. The hexane extract was rotary evaporated to 61 g of orange oil. This oil was subjected to column chromatography on silica gel starting with 10% of ethyl acetate in hexane. ^{1}H NMR spectrum of the eluted fraction showed that it contained trimethyl orthoformate. Changing the eluent to a mixture of 50% ethyl acetate in hexane gave 56.16 g (80%) of the product after rotary evaporation which was confirmed by ^{1}H NMR ($CDCl_3$): δ 1.99(quintet, J = 7 Hz, 2H); 2.37(two almost coincident triplets, J = 7 Hz, 4H); 3.71(s, 3H); 5.38(s, 1H).

3-Methoxy-2-methyl-2-cyclohexen-1-one, **2b**[10]**:**

Amberlite IR-120(plus)(20.95 g) was stirred for 24 h in absolute methanol. The alcohol was decanted and replaced with 100 mL of fresh absolute methanol. 2-Methyl-1,3-cyclohexanedione(50.66 g, 402.06 mmol), purified by rinsing with absolute ether, and 50 mL of anh. trimethyl orthoformate were added. The suspension was sealed with a rubber septum and stirred at room temperature for five days. The reaction mixture was transferred to a flask and solvents were rotary evaporated until no more distillation was occurring at 100°C bath temperature. The residual liquid was extracted several times with hexane until a loose precipitate of unreacted 2-methyl-1,3-cyclohexanedione weighing 10.64 g was left. The combined hexane extracts was rotary evaporated to obtain 45.91g (82%) of the product; ^{1}H NMR ($CDCl_3$): δ 1.60 (t, J = 1.60 Hz, 3H); 2.00(quintet, J = 7.16 Hz, 2H); 2.34(t, J = 7.16 Hz, 2H); 2.56(t, J = 7.16 Hz, 2H); 3.83(s, 3H).

3-n-Butyl-2-cyclohexen-1-one, **3a**[12]

This compound was the major product from the use of anh. ether as solvent in attempted synthesis of 3-(p-N,N-dimethylaminophenyl)cyclohexenone, **3b** through the generation of p-N,N-dimethyaminophenyllithium from the corresponding aryl bromide and n-BuLi. The aryl bromide was very insoluble in ether, even after the suspension was warmed up to 0°C. When 3-methoxycyclohexenone was added, the unreacted n-BuLi reacted with it as the only nucleophile present. Much of the aryl bromide was recovered. Arylation of the vinologous ester in THF worked because of the better solubility of aryl bromides in THF at low temperatures which allowed the formation of the aryllithium nucleophile. After this observation, this compound was prepared in 89% yield by treating 3-methoxycyclohexenone in anh.ether with n-BuLi by mixing the reactants at -78°C and warming to 0°C. It was purified by column chromatography on silica gel using 20% ether in hexane as eluent. **^{1}H NMR**($CDCl_3$): δ 0.90 – 0.94(t, J = 7.32 Hz, 3H); 1.29 – 1.38(sextet, J = 7.32 Hz, 2H); 1.45 – 1.52(quintet, J = 7.32 Hz, 2H); 1.95 – 2.02(quintet, J = 6.40 Hz, 2H); 2.20 – 2.23(t, J = 7.32 Hz, 2H); 2.27 – 2.30(t, J = 5.96 Hz, 2H); 2.34 – 2.37(t, J = 5.96 Hz,2H); 5.87(s, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 13.83; CH_2: 22.33, 22.72, 29.02, 29.65, 37.35, 37.76; vinyl CH: 125.62; vinyl C with no attached H: 166.76; carbonyl C: 200.00.

3-[(p-N,N-Dimethylamino)phenyl]-2-cyclohexen-1-one, **3b**

A 250 mL 3-necked round bottom flask was flame dried under nitrogen. After cooling to room temperature, the flask was charged with 20.27 g (101.35 mmol) of p-N,N-dimethylaminobromobenzene and appropriate necks of the flask were sealed with rubber septa. Then, 90 mL of tetrahydrofuran (THF) dried over sodium benzophenone ketyl, was added with a syringe. After the reaction mixture has been cooled to-78°C, 74 mL of 1.6 M n-BuLi in hexane was added drop-wise over 10 min. The reaction mixture turned into awhite slurry that was difficult to stir. The slurry was stirred at -78°C for 4.5 h and then, 12 g (95.24 mmol) of freshly distilled 3-methoxycyclohexenone in 20 mL of dried THF was added drop-wise by syringe. By the time the ether solution was added to the reaction mixture, the slurry had turned to a yellow solution with a small amount of white solid suspension. The reaction was allowed to warm up to 0°C in 3 h. The reaction mixture was re-cooled to -30°C using dry ice/acetone and then, 25 mL of saturated $NH_4Cl_{(aq)}$ was added. After warming up to room temperature, the cake which was formed thawed and stirring resumed. The THF was distilled off on a rotary evaporator and to the residual suspension was added 10 mL of conc. HCl acid diluted to 40mL with distilled water. The reddish solution formed was refluxed at 80°C, bath temperature, for 6 h and left to cool to room temperature. The aqueous solution was carefully neutralized with solid $NaHCO_3$ and the thick brown suspension was suction-filtered. The solid product was rinsed with small portions of water after which it was dissolved in CH_2Cl_2. The CH_2Cl_2 was dried over anhydrous $MgSO_4$. Rotary evaporation of the dried, filtered product solution gave 18.74 g of the crude product. The crude product was applied to a silica gel column as a hot solution in CCl_4. The upper part of the column was kept warm with a heat gun to avoid crystallization of the product during its application on the column. Elution with 10% ethyl acetate in hexane was continued until eluate was blank by TLC. Then the column was eluted with CH_2Cl_2 to obtain 16.00 g (78%) of the expected product as a yellow solid. **Mp**: 133.7 ^{o}C; **^{1}H NMR**($CDCl_3$): δ 2.12(quintet, J = 6.44 Hz, 2H); 2.46(t, J = 6.44 Hz, 2H); 2.74(t, J = 6.44 Hz, 2H); 3.02(s, 6H); 6.42(s, 1H); 6.69 and 6.72(d, J =

9.16 Hz, 2H, aromatic); 7.50 and 7.52(d, J = 9.16 Hz, 2H, aromatic); **^{13}NMR**($CDCl_3$): CH_2: 22.78, 27.43, 37.22; N-CH_3: 40.12; aromatic and vinyl CH: 111.68, 121.35, 127.48; aromatic and vinyl C with no attached H: 125.07, 151.65, 159.50; carbonyl C: 200.01; **MS**(M/z): 215(M^+, 94); 187(100); 159(75); 115(68); **UV-Vis:** λ_{max} = 371.0 nm; ε= 4.60 x 10^4 $M^{-1}cm^{-1}$ **Elemental analysis**: Calculated: C = 78.10%; H = 7.96%; N = 6.51%; Found: C = 77.78%; H = 8.06%; N = 6.39%.

2-Methyl-3-[(p-N,N-dimethylamino)phenyl]-2-cyclohexen-1-one, 3c:

Magnesium turnings (20 g, 823 mmol) was stirred vigorously under nitrogen at room temperature for 24 h to break up the turnings into smaller pieces and uncover metallic surfaces. To the dark colored chips, 90 mL of anh. THF was added by syringe. Then, p-N,N-dimethylaminobromobenzene (60.11 g, 299 mmol), dissolved in 90 mL of anh. THF was added through a pressure equalizing addition funnel in t10 min. The stirred reaction mixture was refluxed using an oil bath for 24 h during which time the reaction mixture turned from light blue to dark. After cooling to -15°C with an ice-salt bath, 3-methoxy-2-methylcyclohexenone, **2b** (28.00 g, 200 mmol) in 90 mL of anh. THF was added to the Grignard reagent using an addition funnel over a period of 1 h. The bath temperature was maintained between -15°C and -10°C during the addition of the vinylogous ester. The reaction mixture was stirred for 42 h during which time, it warmed up to and remained at room temperature. The reaction solution was decanted from excess Mg chips into another round bottomed flask. After cooling to -10°C, a solution of 20 g of NH_4Cl in 50 mL of distilled water was added to the reaction mixture. The resulting yellow suspension was stirred 24 h as it warmed to room temperature. The insoluble solids were suction-filtered and rinsed with THF until washings were colorless. The combined THF solution was rotary evaporated to a dark liquid. The dark liquid was cooled to -10°C and 30 mL of 12 M HCl acid, cooled to 0°C was added in portions to the stirred crude product. A dark yellow cake formed at the bottom of the reaction flask which re-dissolved after it was broken up and stirred at room temperature. The aqueous acid solution was heated at 80°C for complete dehydration of the alcohol intermediate. After cooling to room temperature, the aqueous acidic solution was carefully neutralized with solid sodium bicarbonate until basic to litmus paper. The product precipitated out of solution as an ash-colored cake. The cake was broken up and suction-filtered. The resulting solid was rinsed with hexane to remove an oily component. The dark gray solid product weighed 40.55 g after vacuum drying. An additional 1.95g of product was obtained from column chromatography of the ether extracts of the aqueous layer on silica gel using a 9:1 ratio of hexane : ethyl acetate respectively. Total mass of product was 42.50 g (93%). Use of n-BuLi to generate the nucleophile resulted in a 77% yield of product. **Mp**: 97.6 ^{o} C; **^{1}H NMR**($CDCl_3$): δ 1.82(s, , 3H); 2.03 – 2.06(quintet, J = 6.40 Hz, 2H); 2.47 – 2.50(t, J = 6.44 Hz, 2H); 2.62 – 2.65(t, J = 5.96 Hz, 2H); 2.99(s,6H); 6.70 and 6.72(d, J = 8.72 Hz, 2H, aromatic); 7.15 and 7.17(d, J = 9.16 Hz, 2H, aromatic); **^{13}NMR**($CDCl_3$): δ CH_3: 13.33; CH_2: 22.64, 32.69, 37.81; N-CH_3: 40.30; aromatic and vinyl CH: 111.48, 128.86; aromatic and vinyl C with no attached H: 128.57, 130.63, 150.10, 156.83; Carbonyl C: 200.29; **MS**(M/z): 229(M^+, 100); 185(52); 158(35); **UV-Vis:** λ_{max} = 343 nm, ε = 2.24 x 10^4 $M^{-1}cm^{-1}$; **Elemental analysis**: Calculated: C = 78.60%; H = 8.30%; N = 6.11%; Found: C = 78.56%; H = 8.44%; N = 6.10%.

7-[(p-N,N-Dimethylamino)phenyl]-2,3,4,4a,5,6-hexahydro-2-naphthalenone, 4a

This compound was prepared using the same procedure as **4b**. Crude product was purified by column chromatography on neutral alumina (Brockman activity III). A 36% product yield was obtained in one run. Analytical sample was obtained by recrystallization with a mixture of chloroform and ethyl acetate. **Mp:** 206.1^{o}C; **^{1}H NMR**($CDCl_3$): δ 1.49 – 1.61 and 1.70 – 1.81(unresolved multiplets, 2H); 2.05 – 2.21(unresolved multiplet, 2H); 2.43 – 2.67(broad and unresolved multiplet, 4H); 2.80 – 2.81 and 2.84 – 2.85(broad and unresolved multiplets, 1H); 3.01(s, 6H); 5.86(s, 1H); 6.60(s, 1H); 6.69 – 6.71(d, J = 9.28 Hz, 2H); 7.46 – 7.49(d, J = 9.28 Hz, 2H); **^{13}C NMR**($CDCl_3$)**:** δ CH_2: 27.90, 29.80, 30.18, 37.91; methine C: 35.50; N-CH_3: 40.20; aromatic and vinyl CH: 111.86, 120.98, 122.67, 126.68; aromatic and vinyl C with no attached H: 140.19, 150.84, 160.11, 189.30; carbonyl C: 199.99. **MS** (M/z): 267 (M^+, 100), 239 (36); 210 (17); 165 (13); 104 (12). **UV-Vis:** λ_{max} = 398 nm (ε = 5.66 x 10^4 $M^{-1}cm^{-1}$), 277 nm (ε = 1.93 x10^4 $M^{-1}cm^{-1}$); **Elemental analysis**: Calculated: C = 80.86%, H = 7.92% and N = 5.24%. Found: C = 80.34%, H = 8.03% and N = 5.11%.

7-[(p-N,N-Dimethylamino)phenyl]-8-methyl-2,3,4,4a,5,6-hexahydro-2-naphthalenone, 4b

A 500 mL round bottom flask bearing a pressure equalizing addition funnel connected to a nitrogen line was flame dried. After cooling, 90 mL of anh. THF was added to the flask and cooled to -78°C by immersion into a dry ice -acetone bath (a yellow color develops if the amine is added to the THF at room temperature). After 6.14 g (60.79 mmol) of diisopropylamine was added to the flask with a syringe, 37 mL of 1.6 M n-BuLi solution in hexane was added in 11 min through the pressure equalizing addition funnel. After 1 h at -78°C, the flask was removed from the bath and allowed to warm up to 0°C. A colorless solution of lithium diisopropylamide (LDA) was obtained. The solution was re-cooled to-78°C and 7.55 g (32.97 mmol) of 2-methyl-3-(p-N,N-dimethylaminophenyl)cyclohexenone, **3c,** dissolved in 60 mL of anh. THF was added over 20 min through the addition funnel. The reaction mixture developed a blue color during the addition. After 2 h 42min at -78°C, the reaction flask was removed from the bath and allowed to warm up to room temperature. The solvent and diisopropylamine formed during the generation of the kinetic enolate were evaporated off using a vacuum pump with a cold finger at -78°C. The resulting white cake, under a stream of nitrogen gas, was dissolved in 210 mL of anh. THF and the blue solution was re-cooled to -78°C. Methyl vinyl ketone (5.20 g, 74.29 mmol), dissolved in 60 mL of anh.THF was introduced into the funnel and added to the enolate in 27 min. As the addition started, the enolate solution changed from blue to yellow. The reaction mixture was stirred overnight as it warmed up to room temperature and the color had changed to orange.

After 20mL of distilled water was added to the reaction mixture and stirred for 4 h, the orange supernatant was decanted from the white solid component of the reaction mixture. The solid was rinsed with ether and the ether rinse was combined with the THF solution and the solvents were removed by rotary evaporation. The residue was extracted with ether (total volume 800mL) and the ether extract was stirred with 20mL of 12 M HCl diluted to 240 mL with distilled water. After 30 min of vigorous stirring, a pink aqueous and light yellow layers separated. The aqueous layer was carefully neutralized by adding solid $NaHCO_3$ and extracted with ether until new extract was colorless. All ether solutions were combined, dried over anh. $MgSO_4$, suction filtered and rotary evaporated to obtain 13.80 g of an orange liquid.

This crude Michael adduct was dissolved in 200 mL of anh.THF in a 500 mL round bottom flask followed by the addition of 10 g (89.29 mmol) of *t*-BuOK. The flask was sealed with rubber septum and the dark orange solution was stirred at room temperature for 5 days. Then, 10 mL of distilled water was added. The mixture was stirred for 24 h; an equal volume of ether was added and stirring was continued for another 24 h. After rotary evaporating off the organic solvents, the residue was stirred with 800 mL of a 1:1 mixture of ethyl acetate: ether solvent mixture. The organic layer was separated and dried over anh. $MgSO_4$ and the filtrate was rotary evaporated to obtain 8.84 g (95%) of the product as a yellow solid. Sample for elemental analysis was obtained by recrystallization from 10% ethyl acetate in hexane. **Mp**: 175.3^{o}C; **^{1}H NMR**($CDCl_3$): δ 1.50 – 1.61(two almost coincident q; J = 12.80 Hz, 1H); 1.70 – 1.82(broad unresolved multiplet, 1H); 1.84(s, 3H); 1.94 – 1.99 and 2.09 – 2.15(unresolved multiplets, 2H); 2.38 – 2.65(broad unresolved multiplet, 5H); 2.99(s, 6H); 6.06(s, 1H); 6.70and 6.73(d, J = 9.20 Hz, 2H, aromatic); 7.10 and 7.08(d, J = 9.20 Hz, 2H, aromatic); **^{13}NMR**($CDCl_3$): δ CH_3: 16.04; CH_2: 30.00, 30.65, 33.24, N-CH_2: 37.56; methine C: 36.31; N-CH_3: 40.40; aromatic and vinyl CH: 111.68, 120.97, 129.15; aromatic and vinyl C with no attached H: 126.90, 130.36, 148.30, 149.71, 161.09; carbonyl C: 200.94; **UV-Vis:** λ_{max}: 366.1 nm; $\varepsilon = 3.10 \times 10^4$ $M^{-1}cm^{-1}$; 288.0 nm; $\varepsilon = 2.89 \times 10^4$ $M^{-1}c$ m^{-1}; **MS**(M/z): 281(M^+, 100), 253 (19), 165(10); **Elemental analysis**: Calculated: C = 81.14%; H = 8.18%; N = 4.98%; Found: C = 80.82%; H = 8.41%; N = 4.78%

9-[(p-N,N-Dimethylamino)phenyl]-10-methyl-2,3,4,4a,5,5a,6,6a,7,8-decahydro-2-tetracenone, 5b

This compound was prepared in 11% yield using the same procedure as **4b** except that four times excess of methyl vinyl ketone, dissolved in a 20 mL of absolute t-BuOH and 90mL of anh. THF was added instead of twice the stoichiometric amount used to obtain **4b**. When the Michael adduct product was subjected to cyclization as in the procedure for **4b**, a red precipitate was formed in the reaction mixture. This red precipitate was filtered out, dissolved in $CHCl_3$ with heat and the solution dried over anh. $MgSO_4$. Suction

filtration and rotary evaporation of the solvent gave the red solid which was triturated with ethyl acetate, a solvent in which it is insoluble, to remove liquid product contaminants. The ^{1}H NMR and other analytical data confirmed the structure of the product. Examination of the liquid component of this cyclization reaction product led to the conclusion that it was a complex mixture of substances and was not processed any further. **Mp**: 300.5 ^{o}C; **^{1}H NMR**($CDCl_3$): δ 1.18 – 1.31(quintet, J = 13.28 Hz, 2H); 1.44 – 1.51(broad quintet, 1H); 1.84(s, 3H); 1.70- 1,80 , 1.89 – 1.99 and 2.07 – 2.10(broad unresolved multiplets, 5H); 2.38 – 2.60(broad unresolved multiplet, 7H); 2.97(s, 6H); 5.79(s, 1H); 6.09(s, 1H); 6.25(s, 1H); 6.70 and 6.72(d, J = 8.24 Hz, 2H, aromatic); 7.06 and 7.08(d, J = 8.24 Hz, 2H, aromatic); **^{13}NMR**($CDCl_3$): δ CH_3: 16.08; CH_2: 30.41, 30.57, 33.15, 37.09, 38.03, 38.10; methane C: 36.12, 36.15, 36.60;N-CH_3: 40.60; aromatic and vinyl CH: 111.90, 121.38, 122.30,123.83, 129.31; aromatic and vinyl C with no attached H: 127.11, 131.34, 143.02, 147.73, 149.33, 150.92, 160.34;carbonyl C: 199.87;**UV** (CH_2Cl_2): λ_{max} = 409 .0 nm (ε = 4.15 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 385.23986 amu; Found: 385.23966 amu.

5-(3-n-Butylcyclohex-2-enyliden)-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione: 6a

3-n-Butylcyclohexenone, **3a** (7.64 g, 50.26 mmol) was mixed with 14.08 g (70.40 mmol) of thiobarbituric acid, 1.70 g (22.08 mmol) of NH_4OAc, 60 mL of anh. CCl_4 and 2 mL of glacial acetic acid in a single neck round bottom flask with a Dean-Stack trap, condenser and under positive nitrogen pressure. The flask was heated to reflux. Distillate was removed from the trap every time it filled up and replaced with fresh solvent. The sequence of distillate run-off followed by solvent replacement in the reaction flask was continued until TLC of the reaction mixture on silica gel using 20% ether in hexane showed no detectable unreacted cyclohexenone. Fresh CCl_4(60 mL) was added to the hot reaction mixture and the reaction flask was removed from the oil bath and allowed to cool down to room temperature. The resulting suspension was transferred to a separatory funnel with the help of additional rinsing of the flask with CCl_4. The suspension was treated with distilled water which put all solids into aqueous solution. The dark orange organic layer was separated and its TLC showed presence of excess thiobarbituric acid. In order to remove unreacted thiobarbituric acid, the organic layer was shaken with a 100 mL of water containing 3.0 g of NaOH. After this treatment, TLC of the CCl_4 solution showed no residual 1,3-diethyl-2-thiobarbituric acid. After the organic layer was dried over anh. $MgSO_4$, suction-filtered and rotary evaporated at up to 98°C, 13.30 g (79%) of product was obtained. **Mp**: 67.71 ^{o}C; **^{1}H NMR**($CDCl_3$): δ 0.92 – 0.95(t, J = 7.32 Hz, 3H); 1.25 – 1.31(two overlapped t, J = 6.88 Hz, 6H); 1.31 – 1.40(sextet, J = 7.32 Hz, 2H); 1.50 – 1.57(quintet, J = 7.32 Hz, 2H); 1.79 – 1.85(quintet, J = 6.40 Hz, 2H); 2.28 – 2.35(quintet, J = 7.8 Hz, 4H); 3.13 – 3.17(t, J = 5.96 Hz, 1H); 4.47 – 4.54(two overlapping quintets, J = 6.88 Hz, 4H); 7.99(s, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 12.50, 13.84; CH_2: 22.34, 22.54, 29.74, 29.92, 30.65, 39.87; N-CH_2: 43.44, 43.52; vinyl CH: 124.58; vinyl carbons with no attached H: 112.02, 160.57,161.00, carbonyl carbon: 168.89, 171.78; thiocarbonyl C: 178.37; **MS**(M/z): 334(M^+ , 52), 301(100), 277(14); **UV** ($CHCl_3$): λ_{max} = 376.0 nm (ε = 3.93 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 334.171500 amu; Found: 334.170700 amu.

2-(3-n-Butylcyclohex-2-enyliden)malononitrile: 6b

This compound was prepared by condensing **3a** with malononitrile using 1-methyl-3-octylimidazolium tetrafluoroborate as solvent. **^{1}H NMR**($CDCl_3$): δ 0.92 – 0.95(t, J = 7.32 Hz, 3H); 1.30 – 1.39(sextet, J = 7.32 Hz, 2H); 1.47 – 1.54(quintet, J = 7.32 Hz, 2H); 1.84 – 1.90(quintet, J = 6.44 Hz, 2H); 2.28 – 2.34(two almost coincident q, J = 6.44 Hz, 4H); 2.71 – 2.74(t, J = 6.44 Hz, 2H); 6.60(weakly resolved quintet, 1H); **^{13}NMR**($CDCl_3$): CH_3: 13.81; CH_2: 21.55, 22.45,29.32, 29.46, 29.88, 38.79; vinyl CH: 120.85; vinyl C with no attached H: 112.42, 113.87166.21; nitrile C: 170.74; **UV** ($CHCl_3$): λ_{max} = 307.0 nm (ε = 2.09 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 200.12674 amu; Found: 200.13044 amu.

5-{3-[(p-N,N-Dimethylamino)phenyl]-2-cyclohexenyliden}-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione, 6c

3-(p-N,N-Dimethylaminophenyl)cyclohexenone **3b** (9.66g, 44.93 mmol) was weighed into a 500mL round bottom flask followed by the addition of 15.00 g (75 mmol) of 1,3-diethyl-2- thiobarbituric acid, 1.71 g (22.08 mmol) of NH_4Cl and 120 mL of anh. CCl_4. Then, 2.5 mL of gl. AcOH was added and the mixture was heated to 110°C with a Dean Stark trap under nitrogen gas. After 2.5 h of reflux,

the wet distillate collected in the trap was run off every time it filled up until a viscous dark mass was left in the reaction flask. The reaction mixture was then heated for 2 h as the bath temperature rose to 140°C. 300 mL of fresh CCl_4 was added to dissolve some of the dark mass and thin layer chromatography of the solution on silica gel with 30% ethyl acetate in hexane showed that the cyclohexenone was no more present in detectable amount. The suspension was allowed to cool to room temperature. The suspension was stirred with a solution of 20 g of K_2CO_3 in 100 mL of distilled water to remove excess thiobarbituric acid. After the suspension was filtered, the dark solid product was rinsed with 600 mL of distilled water. The filtrate consisting of both aqueous and organic layers was reserved. The solid product was vacuum-dried for 2 days at room temperature and weighed 15.30 g. The CCl_4 layer of the filtrate was separated and the aqueous layer was extracted with CCl_4 after being saturated with solid NaCl. The combined CCl_4 extracts was dried over anh. $MgSO_4$. Rotary evaporation and stirring of the resulting solid with 50 mL of CCl_4 at room temperature for 12 h led to an additional 2.37 g of product for a total of 17.67 g (~ 100%). **Mp**: 225.8^o C; **^{1}H NMR**($CDCl_3$): δ 1.32(t, J = 6.44 Hz, 3H); 1.92(quintet, J = 6.44 Hz, 2H); 2.77 – 2.80(t, J = 5.96 Hz, 2H); 3.07(s, 6H); 3.23 – 3.26(t, j = 6.40 Hz, 2H); 4.52 – 4.58 (multiplet, 4H); 6.69 and 6.71(d, J = 9.16 Hz, 2H aromatic); 7.71 and 7.74(d, J= 9.16 Hz, 2H, aromatic); 8.96(s, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 12.57; N-CH_3: 40.05; CH_2: 22.67, 27.53, 31.41; N-CH_2: 43.47; aromatic and vinyl CH: 111.67, 121.64, 128.95; aromatic and vinyl C with no attached H: 109.71, 125.83, 152.38, 161.04, 161.20, 162.28; thiocarbonyl C: 173.25; carbonyl C: 178.02; **MS**(M/z): 397(M^+, 55); 395(100); 364(45); 309(30);277(16); **UV** ($CHCl_3$): λ_{max} = 551.0 nm (ε = 4.58 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 397.1823992 amu; Found: 397.183151 amu

2-[3-(p-N,N-Dimethylaminophenyl)cyclohex-2-enyliden]malononitrile, **6d**

3-(p-N,N-Dimethylaminophenyl)cyclohexenone **3b** (5.03 g, 23.40 mmol) was mixed in a round bottom flask with 4.32 g (65.45 mmol) of malononitrile, 0.93 g(12.08 mmol) of NH_4Cl, 50 mL of anh. CCl_4 and 0.5 mL of gl. AcOH and the mixture was heated to 110°C with a Dean Stark trap under nitrogen gas. The process of distillate removal/fresh solvent replenishment was continued until TLC on silica gel with 20% ethyl acetate in hexane showed immensely diminished unreacted cyclohexenone. CCl_4 was first used to dissolve the residue in the hot reaction flask. The dark red solution was decanted into an Erlenmeyer flask and the remaining solid in the flask was scraped with a spatula and transferred into the flask and enough THF was added to put all solid into solution. This organic solution of the product was stirred with distilled water. After separating and rotary evaporation of the organic layer, the solid residue was heated with ethyl acetate. On decanting the red solution and leaving to cool down, 0.64 g of pure product was obtained. The remainder of the crude solid product was subjected to column chromatography on silica gel using a 7:3 (v/v) of ethyl acetate-to-hexane respectively. Through a series of extractions and recrystallizations of the solid from chromatography using ethyl acetate, a total of 3.25 g (53%) of purified product was collected. **Mp**: 204.5^o C; **^{1}H NMR** ($CDCl_3$): δ 2.01(quintet, J = Hz, 2H); 2.81(t, J = Hz, 4H); 3.11(s, 6H); 6.70 and 6.75(d, J = Hz, 2H, aromatic); 7.18(s, 1H); 7.61 and 7.66(d, J = Hz, 2H, aromatic). **^{13}NMR**($CDCl_3$): δ CH_2: 21.68, 27.51, 29.25; N-CH_3: 40.03; aromatic and vinyl CH: 111.69, 116.42, 128.22; aromatic and vinyl C with no attached H: 114.05, 120.72, 123.96, 151.78, 157.70, nitrile C: 170.04; **UV** (CH_2Cl_2): λ_{max} = 469.0 nm (ε = 4.19 x 10^4 $M^{-1}cm^{-1}$); **Elemental analysis**: Calculated: C = 77.57% ; H = 6.46%; N = 15.97%; Found: C = 76.93%; H = 6.42%; N = 15.99%.

5-{7-[(p-N,N-Dimethylamino)phenyl]-2,3,4,4a,5,6-hexahydro-2-naphthalenyliden}-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione, **7a**

This compound was obtained in quantitative yield by an identical procedure for other 1,3-diethyl-2-thiobarbituric acid adducts. Heating at 110°C for 12 h was necessary for complete reaction of the cyclohexenone as determined by TLC. For this product, the aqueous layer was extracted and processed to isolate additional product. **Mp**: 262.3^{o}C; **^{1}H NMR**($CDCl_3$)**:** δ 1.29 – 1.32(t, J = 6.84 Hz, 6H); 1.43 – 1.63(broad unresolved multiplet, 2H); 2.04 – 2.10(broad unresolved multiplet, 2H); 2.46 – 2.51(broad triplet, J = 12.38 Hz,1H); 2.61 – 2.68(broad unresolved triplet, J = 13.52 Hz, 1H); 2.83 – 2.95(broad unresolved multiplet, 2H); 3.05(s, 6H); 3.73 and 3.78(triplet of doublet, J = 18.80 Hz, 1H); 4.55(broad unresolved multiplet, 4H); 6.68 and 6.70(d, J = 8.72 Hz, 2H,aromatic); 6.92(s, 1H); 7.54 and 7.56(d, J = 8.72 Hz, 2H, aromatic); 8.31(s, 1H); **^{13}C NMR**($CDCl_3$)**:** δ CH_3: 12.56; CH_2: 27.83, 29.72, 29.78, 32.15,

43.50; methine C: 35.71; N-CH_3: 40.14; aromatic and vinyl CH: 111.76, 123.01, 124.98, 127.44; aromatic and vinyl C with no attached H:109.15, .126.10, 151.41, 152.77, 161.08, 164.83; thiocarbonyl C: 172.84; carbonyl C: 177.92; **MS** (M/z): 449 (M^+, 100), 416 (24), 361 (18); ; **UV** (CH_2Cl_2): λ_{max} = 572.0 nm ($\varepsilon = 3.64 \times 10^4$ $M^{-1}cm^{-1}$). The above proton and C-13 and MS spectra are consistent with the structure of the condensation product formed between thiobarbituric acid and the dienone **4a** whose structure was confirmed by elemental analysis before use.

{7-[(p-N,N-Dimethylamino)phenyl]-2,3,4,4a,5,6-hexahydro-2-naphthalenyliden}malononitrle, 7b

The bicyclic ketone **4a** (0.10 g, 0.36 mmol), malononitrile (0.21 g, 3.18 mmol), 2.14 g of the ionic liquid, 1-methyl-3-n-octylimmidazolium hexafluoroborate and 15 drops of pyridine were sealed with a rubber septum in a 50 mL round bottom flask and heated on an oil bath to 80°C for 3 h. Then the bath temperature was raised to 98°C and maintained for 26 h. TLC of the reaction mixture showed only trace amount of the ketone.

The reaction mixture was extracted with ether continuously until extracts were colorless. The solution was left in the fridge for 12 h to force out from solution dissolved ionic liquid. After decanting the cold solution from a small amount of viscous ionic liquid, the solvent was rotary evaporated. The crude product was re-dissolved in chloroform and the solution was stirred with aqueous solution of Na_2CO_3 to remove excess malononitrile. The organic layer was washed with distilled water, dried over anh. $MgSO_4$, suction-filtered and rotary evaporated to obtain 0.14 g of a dark solid after two days on the vacuum pump at room temperature. The crude product was subjected to column chromatographic purification on silica gel with chloroform. The recovered black solid from rotary evaporation and drying in a vacuum pump weighed 0.09 g (76%). **Mp**: 235.7°C; **^{1}H NMR**($CDCl_3$)**:** δ 1.45 – 1.59 (broad unresolved multiplet, 2H); 2.06 – 2.12(unresolved multiplet of a doublet, J = 12.80 Hz, 2H); 2.44 – 2.69(unresolved multiplet, 3H);2.87 – 2.90, 2.92 – 2.94 and 3.02 – 3.08(unresolved multiplets, 2H); 3.04(s, 6H); 6.60(s, 1H); 6.69 and 6.71(d, J = 8.94 Hz, 2H, aromatic); 6.72(s, 1H); 7.52 and 7.50 (d, J = 8.94 Hz; 2H, aromatic); **^{13}C NMR**($CDCl_3$)**:** δ CH_2: 27.89, 28.83, 29.63, 29.73; methine C: 35.87; N-CH_3: 40.25; aromatic and vinyl CH: 111.88, 119.38, 120.89, 127.25; aromatic and vinyl C with no H: 113.80, 114.52, 125.86, 151.32, 151.79, 159.45; nitrile C: 169.92; **UV** (CH_2Cl_2): λ_{max} = 499.0 nm ($\varepsilon = 4.58 \times 10^4$ $M^{-1}cm^{-1}$). The proton and C-13 spectra are consistent with the structure of the condensation product between malononitrile and the dienone **4a** whose structure was confirmed by elemental analysis before use.

5-{7-[(p-N,N-Dimethylamino)phenyl]-8-methyl-2,3,4,4a,5,6-hexahydro-2-naphthalenyliden}-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione, 7c

This compound was prepared from dienone **4b** in quantitative yield using the same procedure as the 1,3-diethyl-2- thiobarbituric acid adduct of 3-(p-N,N-dimethylaminophenyl)cyclohexenone. For this reaction, the temperature was raised to 130°C after much of the solvent had distilled off through the Dean-Stark trap. TLC, on alumina with 20% ethyl acetate in hexane, of the reaction mixture after 1 h at this temperature showed complete disappearance of the cyclohexenone. Stirring the CCl_4 solution of the product with aqueous $NaHCO_3$ yielded a product that required no further purification. Drying was carried out with anh. Na_2SO_4 instead of anh. $MgSO_4$ because it did not retain some of the product. This compound has good solubility even in hexane. **Mp**: 184.7 °C; **^{1}H NMR**($CDCl_3$): δ 1.25 – 1.32(two almost coincident triplets, J = 6.98 Hz. 6H), 1.42 – 1,59(sextet, J = 12.80 Hz, 2H); 1.75 – 1.83, 1.89 – 1.98 and 2.06 – 2.07(broad unresolved multiplets, 2H); 2.03(s, 3H);2.38- 2.89(broad unresolved multiplet, 4H); 3.01(s, 6H); 3.70 – 3.75(triplet of doublet, J = 18.76 Hz, 1H); 4.44 – 4.63, multiplet with 12 lines, J = 6.88 Hz, 4H); 6.71 and 6.74(d, J = 8.72 Hz, 2H, aromatic); 7.13 and 7.15(d, J = 8.72 Hz, 2H, aromatic); 8.47(s, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 12.58, 16.59; CH_2: 29.71, 30.24, 31.84, 33.30; N-CH_3: 40.34; N-CH_2: 43.53; methine C: 36.56; aromatic and vinyl CH: 111.53, 122.05, 129.50; aromatic and vinyl C with no attached H: 110.91, 129.19, 149.82, 152.52, 160.91, 161.18, 164.39; thiocarbonyl C: 173.43; carbonyl C: 178.13; **MS**(M/z): 463(M^+, 25), 430(7), 214(44), 200(89), 129(100); **UV** (CH_2Cl_2): λ_{max} = 501.0 nm ($\varepsilon = 2.10 \times 10^4$ $M^{-1}cm^{-1}$); **HRMS**: Calculated: 463.229349 amu; Found: 463.228394 amu.

{7-[(p-N,N-Dimethylamino)phenyl]-8-methyl-2,3,4,4a,5,6-hexahydro-2-naphthalenyliden}malononitrile, 7d

The bicyclic ketone **4b** (0.10 g, 0.36 mmol), malononitrile (0.34 g, 5.15mmol), 2.23 g of ionic liquid and 10 drops of pyridine were mixed in a 25 mL round bottom flask. The flask was sealed with a rubber septum and heated in an oil bath. All solids dissolved in the ionic liquid at 75°C and the bath temperature was maintained at 98°C for 24 h after which time, TLC (silica gel, $CHCl_3$) of the reaction mixture showed only trace of the substrate ketone. The reaction mixture was extracted with ethyl acetate and the extract was treated with aqueous Na_2CO_3 to remove excess malononitrile. The organic layer was dried over anh. $MgSO_4$, suction filtered and rotary evaporated to yield 0.81 g of a red oil which TLC showed to contain product in ionic liquid. Column chromatography on alumina (Brockman Activity 1) with $CHCl_3$ and solvent removal produced an orange red oil. This red oil was extracted with ether and rotary evaporation of the ether solvent left an orange-red oily solid. The solid was stirred with hexane, suction-filtered and vacuum-dried at room temperature to obtain 0.02 g (17%) of product. The elution on alumina was slow and the column seemed to have retained much of the material applied on the column. The alumina may also have been too active for the compound and may have induced decomposition of much of the product before it could elute from the column. **Mp:** 183.0^{o}C; **^{1}H NMR**($CDCl_3$)**:** δ 1.47 – 1.60 (broad unresolved multiplet, 2H); 1.94(s, 3H); 1.95 – 1.99 and 2.06 – 2.12(unresolved multiplets, 2H);2.44 – 2.73(broad unresolved multiplet, 4H); 3.0(s, 6H); 3.05 – 3.11(unresolved multiplets of a doublet, J = 16.96 Hz, 1H); 6.70 and 6.73(d, J = 8.94 Hz, 2H, aromatic); 6.77(s, 1H); 7.09 and 7.12 (d, J = 8.94 Hz; 2H, aromatic); **^{13}C NMR**($CDCl_3$)**:** δ CH_3: 16.19: CH_2: 29.32, 29.43, 29.61, 33.20; methine C: 36.69; N-CH_3: 40.31; aromatic and vinyl CH: 111.52, 116.92, 129,59; aromatic and vinyl C with no H: 113.33, 114.16, 127.30; 129.59, 150.03, 152.27, 160.35; nitrile C: 170.96; **UV** (CH_2Cl_2): λ_{max} = 454.0 nm ($\varepsilon = 2.26 \times 10^4$ $M^{-1}cm^{-1}$). The proton and C-13 spectra are consistent with the structure of the condensation product between malononitrile and the dienone **4b** whose structure was confirmed by elemental analysis before use.

5-{9-[(p-N,N-Dimethylamino)phenyl]-8-methyl-2,3,4,4a,5,5a,6,6a,7,8-decahydro-2-tetracenyliden}-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione, 8c

The tetracyclic tetraene-2-one, **5b** (0.12 g, 0.34 mmol), 1,3-diethyl-2- thiobarbituric acid (0.67 g, 3.35 mmol), 2.3 g of ionic liquid and 15 drops of pyridine were sealed in a 50 mL round bottom flask with a rubber septum. The heterogeneous mixture was stirred as bath temperature rose to 100°C. At this temperature, the reaction mixture appeared to be a viscous solution. The starting ketone was no more observable by TLC (silica gel, $CHCl_3$) after 6 h of reaction. The reaction mixture was extracted with a total of 400 mL of ether in portions until extract of the residue was colorless. The combined ether extracts was treated with aqueous sodium bicarbonate to remove excess thiobarbituric acid. The resulting dark solid obtained after drying, filtering and rotary evaporation of the ether solution was chromatographed on silica gel with CH_2Cl_2 to obtain 0.12g (67%) of adduct. **Mp**: 262.2 ^{o}C; **^{1}H NMR**($CDCl_3$): δ 1.25 – 1.31(t, J = 6.88 Hz, 6H); 1.22 – 1.32(unresolved multiplet, 2H); 1.43 – 1.57(unresolved multiplet, 2H); 1.88(s, 3H); 1.91 – 2.05(broad unresolved multiplet, 4H); 2.52 – 2.66(broad unresolved multiplet, 4H); 2.81 – 2.91(unresolved multiplet, 2H); 2.99(s, 6H); 3.71 – 3.75(two unresolved triplets, 1H); 4.54(broad singlet, 4H); 6.33(two coincident singlets, 2H); 6.71 and 6.73(d, J = 8.46 Hz, 2H, aromatic); 7.08 and 7.10(d, J = 8.46 Hz, 2H, aromatic); 8.22(s, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 12.57, 16.14; N-CH_3:40.45; CH_2: 29.80, 29.92, 30.42, 33.25, 37.04, 37.96; N-CH_2: 43.49; methine C: 36.25, 36.78, 36.94; aromatic and vinyl CH: 111.81, 122,18, 125.14, 126.68, 129.38; aromatic and vinyl C with no attached H: 109.31, 127.52, 129.34, 131.00, 145.28, 149.51, 150.84,155.67, 164.59; carbonyl C: 172.22;thiocarbonyl C: 177.94; **UV** ($CHCl_3$): λ_{max} = 574.0 nm ($\varepsilon = 5.28 \times 10^4$ $M^{-1}cm^{-1}$); **HRMS**: Calculated: 567.29126 amu; Found: 567.29066 amu.

{9-[(p-N,N-Dimethylamino)phenyl]-10-methyl-2,3,4,4a,5,5a,6,6a,7,8-decahydro-2-tetracenyliden}malononitrile, 8d

This reaction was carried out using chloroform as solvent because the tetracyclic tetraen-2-one **5b** dissolved in this solvent at room temperature. N-Methylpyrrolidine was used as amine base with gl. acetic acid and the reaction mixture was refluxed with a Dean-Stark trap for the usual take-off of distillate and replenishment of solvent. After 30 h as temperature rose from 100 -110°C, the starting ketone was still observed in the TLC of the reaction mixture. The reaction mixture was transferred to a separatory funnel and washed

with saturated aqueous $NaHCO_3$ solution. The organic layer was washed with distilled water, dried over anh.$MgSO_4$, suction-filtered and rotary evaporated. The resulting dark solid was chromatographed on silica gel with $CHCl_3$ to obtain 0.16 g (29%) of a shiny dark solid. **Mp**: 263.4 ^{o} C; **^{1}H NMR**($CDCl_3$): δ 1.20 -1.31(octet, J = 7Hz, 2H); 1.47 – 1.54(broad unresolved multiplet, 2H); 1.87(s, 3H); 1.90 – 2.07(broad multiplet, 4H); 2.50 – 2.60(unresolved multiplet, 6H); 2.98(s, 6H); 3.00 – 3.05(unresolved multiplet of a doublet, J = 18.36 Hz, 1H); 6.16(s, 1H); 6.30(s, 1H); 6.52(s, 1H); 6.70 and 6.72(d, J = 8.72 Hz, 2H, aromatic); 7.07 and 7.09(d, J = 7.72 Hz, 2H, aromatic); **^{13}NMR**($CDCl_3$): δ CH_3: 16.14; CH_2: 28.92, 29.69, 30.43, 33.19, 36.80; 37.91; methine C: 36.29, 36.43, 36.77;N-CH_3: 40.56; aromatic and vinyl CH: 111.82, 119.10, 121.50, 124.04, 129.22; aromatic and vinyl C with no attached H: 113.77, 114.56, 127.28, 130.93,144.90, 149.46, 150.25, 154.74, 159.48; nitrile C: 169.46; **UV** (CH_2Cl_2): λ_{max} = 496.0 nm (ε = 5.54 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 433.2521 amu; Found: 433.2521 amu.

5-(3-Methylcyclopenten-2-enyliden)-1,3-diethyl-2-thioxohexahydro-4,6-pyrimidinedione, 11a

This thiobarbituric acid adduct was obtained by a procedure that is identical to the preparation of the cyclohexenone analog **6a**. This product was, however, purified by vacuum-assisted (aspirator) filtration over a short bed of silica gel using a 10% mixture of ethyl acetate in CCl_4 until only a red top layer was left on the silica gel. Rotary evaporation of the eluate, heating up to 102^{0}C bath temperature, gave 12.12 g (80%) of adduct as a yellow solid. **Mp**: 147.9^{o}C; **^{1}H NMR**($CDCl_3$): δ 1.27 – 1.31(two almost coincident t, J = 7.44 Hz, 6H); 2.27(s, 3H); 2.67 and 2.68(d, J = 3.68 Hz, 2H); 3.48 – 3.49(unresolved multiplet, 2H); 4.51 – 4.57(two almost coincident q, J = 6.88 Hz, 4H); 8.02(s, 1H); **^{13}C NMR**($CDCl_3$):δ CH_3: 12.39, 12.41, 19.63; CH_2: 37.92, 37.97; N-CH_2: 43.28, 43.38; vinyl CH: 133.35; vinyl C with no attached H: 108.05, 160.28, 161.01; Carbonyl C: 178.68, 181.54; thiocarbonyl C: 188.49; **MS**(M/z): 278(M^+, 100); 245(99); 190(22); 120(56); **UV** ($CHCl_3$): λ_{max} = 366.1.0 nm (ε = 4.68 x 10^4 $M^{-1}cm^{-1}$); **HRMS**: Calculated: 278.108899 amu; Found: 278.109451 amu.

2-(3-Methylcyclopent-2-enylidene)malononitrile, 11b

The procedure was identical to the procedure described for the maloninitrile adduct of 3-n-butylcyclohexenone **6b**. But due to the better solubility property of the adduct, extraction of the crude product with ether produced 71% of pure product. THF solution of a gummy residue from the ether extraction showed presence of additional product that could possibly be isolated through column chromatography. But that was not explored. **Mp**: 89.2^{o}C; **^{1}H NMR**($CDCl_3$): δ 2.18 – 2.19 (d, J = 0.92 Hz, 3H); 2.77 – 2.79(broad unresolved multiplet, 2H); 3.01 – 3.03(unsymmetrical t; 2H); 6.56(weak splitting, 1H); **^{13}NMR**($CDCl_3$): δ CH_3: 18.88; CH_2: 32.63, 37.91; vinyl CH: 128.62; vinyl C with no attached H: 112.94, 113.48, 176.09; nitrile C: 185.78; **MS**(M/z): 144(M^+, 70); 129(58); 116(42); 79(100); **UV** ($CHCl_3$): λ_{max} = 301.0.0 nm (ε = 2.55 x 10^4 $M^{-1}cm^{-1}$); **Elemental analysis**: Calculated: C = 74.98; H = 5.59; N= 19.43; Found: C = 75.16; H = 5.70; N = 19.32.

Acknowledgements

The authors thank the United States Office of Naval Research (ONR Grant # N00014-98-1-0486 and N00014-00-1-0864) and National Science Foundation (NSF MRI Grant # 0722510) for financial support for this work. We are grateful to Mr. Kim Harich of the Biochemistry Department and Dr. Mehdi Khorassani of the Chemistry Department, all at Virginia Polytechnic and State University (Virginia Tech), Blacksburg, VA, U.S.A. for both nominal and exact mass spectral analyses.

References

1. (a) Dagani Ron (1996) Devices Based On Electro-optic Polymers Begin To Enter Marketplace: Commercialization is spurred by recent dramatic improvements in material's stability and optical nonlinear-ity. Chem Eng News 74: 22-27. (b) Dalton LR, Harper AW, Ghoan R, Steier WH, Ziari M, et al. (1995) Synthesis and Processing of Improved organic Second-Order Nonlinear Optical Materials for Applications in Photonics. Chem Mater 7: 1060-1081.(c) Moylan CR, Twieg RJ, Lee VY, Swanson SA, Betterton KM, et al. (1993) Nonlinear optical chromophores with large hyperpolarizabilities and enhanced thermal stabil-ities. J Am Chem Soc 115: 12599-12600. (d) Gilmour S, Montgomery RA, Marder SR, Cheng LP, Jen A, et al. (1994) Synthesis of Diarylthio-barbituric aacid Chromophores with Enhanced Second-order Optical Nonlinearities and thermal Stability. Chem Mater 6: 1603-1604.

2. Barzoukas M, Blanchard-Desce M, Josse D, Lehn JM, Zyss J (1989) Very large quadratic nonlinearities in solution of two push-pull polyene series: Effect of the conjugation length and of the end groups. Chem Phys 133: 323 -329.

3. (a) Cheng LT, Tam W, Marder SR, Stiegman AE, Rikken G, Spangler CW (1991) Experimental investigations of organic molecular nonlinear optical polarizabilities. 2. A study of conjugation dependences. J Phys Chem 95: 10643 - 10652. (b) Chen LT, Tam W, Stevenson SH, Meredith GR, Rikken G, Marder SR (1991) Experimental investigations of organic molecular nonlinear optical polarizabilities. 1. Methods and results on benzene and stilbene derivatives. J Phys Chem 95: 10631 - 10643.

4. (a) Dalton LR, Harper AW, Robinson BH (1997) The role of London forces in defining noncentrosymmetric order of high dipole moment-high hyperpolarizability chromophores in electrically poled polymeric thin films. Proc Natl Acad USA 94: 4842 - 4847. (b) Zhang C, Ren AS, Wang F, Zhu J, Larry R, et al. (1999) Synthesis and Characterization of Sterically Stabilized Second-Order Nonlinear Optical Chromophores. Chem Mater 11: 1966 - 1968 (c) Chen J, Zhu j, Harper AW, Wang F, He M, et al. (1997) Synthesis and Characterization of High-μβ Chromophore Containing the Isophorone Moiety for Electro-Optic Applications. Polym Prepr 38: 215 - 216. (d) Meredith GR, VanDusen TG, Williams DJ (1982) Optical and nonlinear optical characterization of molecularly doped thermotropic liquid crystalline polymers. Macromolecules 15: 1385 - 1389.

5. (a) Shu CF, Tsai WJ, Jen AKY (1996) A new synthetic approach for nonlinear optical chromophores possessing enhanced thermal stability. Tet Lett 37: 7055 - 7058. (b) Shu CF, Tsai WJ, Chen JY, Alex KYJ, Zhang Y, et al. (1996) Synthesis of second-order nonlinear optical chromophores with enhanced thermal stability and nonlinearity: a conformation-locked trans-polyene approach. J Chem Soc Chem Commun 2279 - 2280.

6. Shu CF, Shu YC, Gong ZH, Peng SM, Lee GH, Jen AKY (1998) Non-linear Optical Chromophores with Configurationally-Locked Polyenes Possessing Enhanced Thermal Stability and Chemical Stability. Chem Mater 10: 3284 -3286.

7. Ermer S, Lovejoy SM, Leung DS, Warren H, Moylan CR, et al. (1997) Synthesis and Nonlinearity of Triene Chromophores Containing the Cyclohexene Ring Structure. Chem Mater 9: 1437 - 1442.

8. Shu YC, Gong ZH, Shu CF, Eric M, Breitung, et al. (1999) Synthesis and Characterization of Nonlinear Optical Chromophores with Conformationally Locked Polyenes Possessing Enhanced Thermal Stability. Chem Mater 11: 1628 - 1632.

9. (a) Brooke LGS, Craig AC, Haseltine DW, Jenkins PW, Lincoln LL (1965) Color and Constitution. XIII. Merocyanines as Solvent Property Indicators. J Am Chem Soc 87: 2443 - 2450. (b) Knoevenagel E, Herz A (1904) Condensation von Zimmtaldehyd mit Malonester und Acetylaceton. Ber 37: 4483- 4484.

10. (a) Nagaoka H, Shibuya K, Kobayashi K, Miura I, Muramatsu M, Yama-da Y (1993) Synthesis of Optically Active Bicyclo[2.2.2]octanes. Substitution Effect of the Cyclohexenone Ring on the Sequential Michael Reaction Tet Lett 34: 4039 - 4042. (b) Taskinen E (1985) On the Extent of p- p-π−π Conjugation in Some β−Alkoxy-Substituted α,β−Unsaturated Ketones;. Acta Chem Scand B 39: 485 - 488. (c) Taskinen E, Mukkala VM (1982) Thermodynamics of Vinyl Ethers - XXVII. Thermodynamic Stability of β−Methoxy-substituted α,β−Unsaturated Ketones and the Corresponding Carboxylic Esters. Tetrahedron 38: 613 - 616. (d) Dau-phin G, Gourcy JG, Veschambre H (1992) Microbiological Synthesis of Optically Active (2R, 3S)-2,3-Methyl-3-deuteriocyclohexan-1-one. Enantiospecific Anti-Addition of Hydrogen to the Double Bond of Cyclohex-2-en-1-one. Tetrahedron Asymmetry 3: 595-598.

11. Bhosale RS, Bhosale SV, Bhosale SV, Wang T, Zubaidha PK (2004) Iodine-catalyzed synthesis of β−keto enol ethers. Tet Lett 45: 7187-7188.

12. Mudryk B, Cohen T (1993) Generation, some synthetic uses, and 1,2-vinyl rearrangements of secondary and tertiary homoallyllithiums, including ring contractions and a ring expansion. Remarkable accel-eration of the rearrangement by an oxyanionic group. J Am Chem Soc 115: 3855 - 3865**.**

13. White KB, Reusch W (1978) The Synthesis of Bicyclo [2.2.2] octan-2-ones by Sequential Michael Reactions. Tetrahedron 34: 2439-2443.

14. Jones G (1967) In: Adams R, Blatt AH, Boekelheide V, Caims TL, Cope A.C, Cram DJ, House HO, (Editors), Organic Reactions. (15), John Wiley & Sons, New York 205 -599.

15. (a) Mortani Y, Appella DH, Jurkauskas V, Buchwald SL (2000) Syn-thesis of β-Alkyl Cyclopentanones in High Enantiomeric Excess via Copper-Catalyzed Asymmetric Conjugate Reduction. J Am Chem Soc 122: 6797 – 6798. (b) Tuttle JB, Ouellet SG, Macmillan DWC (2006) Organocatalytic Transfer Hydrogenation of Cyclic Enones. J Am Chem Soc 128: 12662 - 12663.

16. (a) Gorman CB, Marder SR (1993) An investigation of the interrelation-ships between linear and nonlinear polarizabilities and bond length alternation in conjugated organic molecules. Proc Natl Acad Sci USA 90: 11297 – 11301. (b) Marder SR., Cheng LT, Tiemann BG, Friedli AC, Blanchard-Desce M, et al. (1994) Large First Hyperpolarizabilities in Push-Pull Polyenes by Tuning of Bond Length Alternation and Aromaticity Science 263: 511 - 514.