Journal of Thermal Analysis, Vol. 46 (1996) 1133-1150

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

EVALUATION OF THE THERMAL STABILITY OF SOME NONLINEAR OPTICAL CHROMOPHORES

*R. B. Prime, G. Y. Chiou and R. J. Twieg**

IBM Storage Systems Division, San Jose, CA 95193
*IBM Research Division, Almaden Research Laboratory, San Jose, CA 95120, USA

Abstract

Optical data storage is poised to benefit from a new class of advanced polymeric materials engineered to exhibit photorefractivity. Likewise, the transmission and processing of data will also benefit from a related class of materials with electro-optic activity. Organic chromophores are critical constituents of these materials which function due to a change of index of refraction in response to an electric field. However, a number of materials and processing problems remain to be solved before devices incorporating these optically nonlinear chromophores are practical. For example, for electrooptical applications the NLO waveguide should be able to withstand short duration processing temperatures in excess of 300°C and long duration use temperatures of at least 80°C. The requirement for thermochemical stability follows from the need to implement high T_g matrices to provide stability of the orientational or polar order required for long-term device performance and reliability. As a result, the thermal stability of chromophores is now more closely evaluated in addition to their transparency and optical nonlinearity properties. Some chromophore classes, such as the azo dyes studied here, have attractive properties for these applications but further enhancements in overall properties are needed. Identification of the fundamental chemical processes in thermal decomposition of these dyes should lead to introduction of structural changes which provide better stability. Here thermogravimetric analysis (TGA) coupled with mass spectrometry (TGA/MS) is used to provide an assay of thermochemical stability with an added benefit that insight into the mechanisms of thermal decomposition may by identified. In this initial study diaryl substitution of the amine in derivatives of 4-amino-4′-nitroazobenzene was observed to greatly enhance thermal stability relative to dialkyl substitution. Substitution of phenyl for alkyl eliminates structural features involved in the most facile degradation mechanism available to the alkyl derivative.

Keywords: NLO chromophores, photorefractive materials, TGA/MS, thermal stability, thermogravimetric analysis-mass spectrometry

Introduction

The nonlinear optical (NLO) chromophore is the molecular species responsible for imparting optical nonlinearity to the bulk NLO media and for second order nonlinearity the chromophores themselves are optically anisotropic and

0368-4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

are arranged in the bulk in a net acentric and polar fashion. These special molecules are described as 'chromophores' because they are often highly colored dyes which absorb in the visible region of the electromagnetic spectrum. Over the last two decades significant progress has been made in identifying, measuring and optimizing the basic physical properties of these highly specialized chromophores. Once the more salient properties had been identified the optimization process then evolved to dealing with tradeoffs of one desirable property with another (such as microscopic nonlinearity with thermal stability or microscopic nonlinearity with transparency, etc.). As a result, NLO chromophores now comprise a broad collection of chemical structures which have been optimized for application in a range of diverse formats including single crystal, glassy monomer, glassy polymer, liquid crystal monomer, liquid crystal polymer and Langmuir-Blodgett film [1]. No single chromophore or even class of chromophores satisfies all the specific requirements of all these formats and their potential applications.

The thermal stability of chromophores is recognized to be a particularly important consideration for applications in electro-optic modulators [2] dictated by demands for long-term device performance and reliability [3]. The field of photorefractive polymer materials and devices is very new and the material and device parameters and properties are not as yet well defined [4]. In order to be useful in projected electro-optic devices, the poled polymer (in which acentric polar order has been created by application of an external electric field which orients the chromophores) should retain a significant fraction of its initial polar order (as is related to the bulk nonlinear optical susceptibility). The polymer and chromophore must survive long-term use temperatures of 80 to 100°C for more than 5 years and short-term processing temperatures as high as 250°C for less than 1 h for poling and/or packaging procedures. Even higher processing temperatures (above 300°C) may be preferable in order to further maximize the temporal stability of poled order and the related electro-optic coefficient. The temporal stability of the polar order appears to be related to the difference between the glass transition of the medium and its use temperature [5]. The larger this temperature difference is the better the stability of the poled order parameter will be. Sub-T_g relaxations are a particularly critical issue for second order nonlinear optical polymers in which the polar order of chromophores has been created by electric field poling near the glass transition temperature of the host matrix. Efforts are underway to employ very high glass transition media, such as certain polyimides, to maximize this temperature difference [6, 7]. Since these systems must be processed at or near the T_g of these high temperature thermoplastic matrices, special chromophores must be found which can withstand these temperatures and still retain the other requisite optical properties.

Nonlinear optical chromophores are usually composed of a conjugated π-system terminated by an electron donating group at one end and an electron accepting group at the other. Among the many possible combinations of structural constituents the amine donor, nitro acceptor and the azobenzene π-system are all very common and, for example, the most widely used chromophore for electro-optic applications to date is Disperse Red 1 (4-N-ethyl-N-(2-hydroxyethyl)-4′-nitroazobenzene, DR1) or some related simple derivative of DR1. However, the thermal instability of some chromophores containing a combination of nitro acceptor and amine donor limits their utility for projected applications. It is of obvious interest to identify the chemical origins of this thermal instability and it appeared that the susceptibility to thermochemical degradation of the amine containing chromophores might be due to an oxidation-reduction reaction of some kind. Because of their polar structure the NLO chromophores possess constituent parts which are readily reduced (e.g., the nitrobenzene functionality) or oxidized (e.g., the aniline functionality). It is well known that nitroaromatic compounds, including nitrobenzene itself, have found wide utility as oxidants in preparative organic chemistry [8]. A molecule which contains both an oxidizing functionality and another functionality which is readily oxidized may thus be particularly susceptible to degradation at elevated temperatures.

In order to identify useful high-temperature chromophores a protocol has been established for the evaluation of thermal stability prior to their incorporation into a device environment [9–14]. Chromophores are first subjected to conventional thermal analysis (DSC and TGA). DSC is often preferred since the

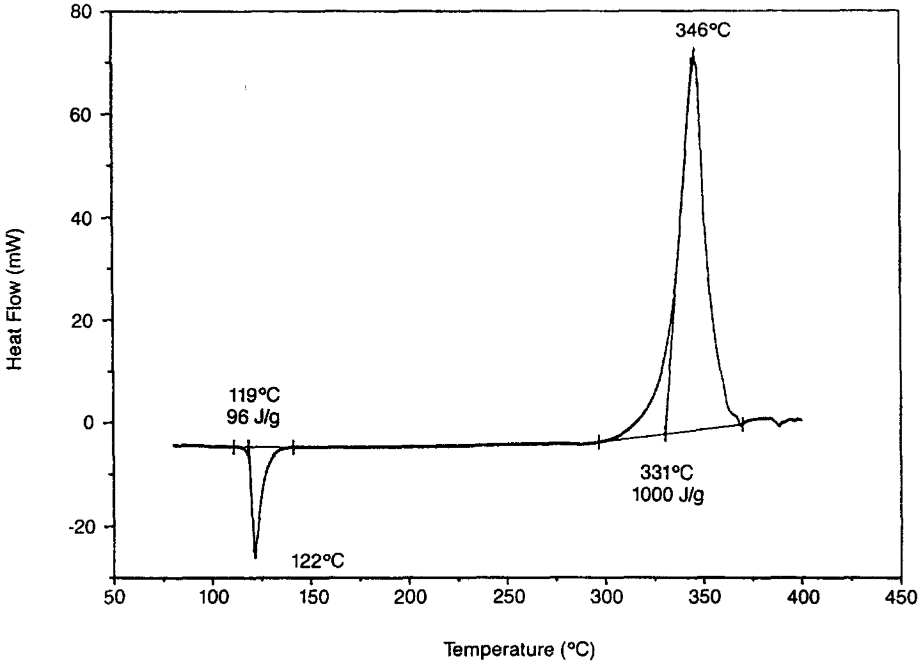


Fig. 1 DSC of 4-N, N-di-*n*-propylamino-4′-nitroazobenzene. Sealed pan with pinhole, 20°C min^{-1} in nitrogen. T_{di}, the extrapolated onset of decomposition, =331°C, and T_{dm}, the maximum decomposition exotherm temperature, =346°C

TGA weight loss is often ambiguous, where decomposition often competes with evaporation or sublimation of the chromophore. In many cases (especially with special donor and acceptor pairs such as amine and nitro) the DSC reveals a clear decomposition exotherm at a temperature T_{di} (defined as the intercept of the exotherm onset tangent with the adjusted baseline, see Fig. 1). The value of

Table 1 The R_1 and R_2 are substituents varied on the donor nitrogen. The onset of decomposition T_{di} is determined by DSC at 20°C min^{-1}; the first oxidation potential E_{pa} is determined in CH_3CN at 200 mV sec^{-1}; the absorption maximum λ_m is determined in $CHCl_3$

R_1	R_2	T_{di} /°C	E_{pa} /V	λ_m /nm
4-(N-H, N-Alkyl)-amino-4′-nitroazobenzenes				
H	H	345	1.09	410
H	Me	324	1.03	448
H	Et	322	1.02	450
H	$CH_2C(CH_3)_3$	324	1.03	454
H	*i*–Pr	341	1.03	454
H	*t*–Bu	365	1.06	456
4-N, N-Dialkylamino-4′-nitroazobenzenes				
Me	Me	308	1.01	480
Et	Et	322	0.99	494
n–Pr	*n*–Pr	331	0.99	496
n–Bu	*n*–Bu	330	0.98	500
Et	CH_2CH_2CN	339	1.12	450
CH_2CH_2CN	CH_2CH_2CN	346	1.25	422
4-(N-Alkyl-N-Aryl)-4′-nitroazobenzenes				
Ph	H	363	1.08	452
Ph	Me	308	1.07	474
Ph	Et	340	1.05	480
Ph	*n*–Bu	340	1.05	484
Ph	Bz	346	1.13	472
Ph	CH_2CH_2CN	345	1.18	442
Ph	*i*–Pr	356	1.08	482
Ph	*c*–C_6H_{11}	346	1.06	486
4-N, N-Diaryl-4′-nitroazobenzenes				
Ph	Ph	393	1.09	486
4–PhPh	4–PhPh	396	1.11	502
4–MeOPh	4–MeOPh	372	0.84	510
4–CF_3Ph	4–CF_3Ph	421	1.34	446

T_{di} is scan rate dependent and it must be emphasized again that the actual practical use temperature for a chromophore will be on the order of at least 50°C and perhaps as much as 100°C less than T_{di}. Based on the previous discussion an attractive candidate NLO chromophore should exhibit T_{di} greater than 350°C, and preferably even above 400°C.

Much of the synthesis and evaluation effort has involved derivatives of 4-amino-4′-nitroazobenzene. This is a particularly useful chromophore class to study because many derivatives are synthetically available [15] and, in fact, some of these chromophores have physical properties which are very attractive for practical application. The properties of a wide range of azodyes (Table 1) have been determined in order to identify and relate trends between specific structural features and thermal stability. Structural modification has concentrated on the amine donor (R_1 and R_2) as it appears to often be the component most susceptible (vide supra) to thermochemical degradation. As is clearly evident from the data in Table 1 a change in substituents on the donor nitrogen can lead to large variation in decomposition onset. The most extreme difference amongst the examples in Table 1 is more than 100° difference between the decomposition onsets for the dimethylamino donor and the bis(4-trifluoromethylphenyl)amino donor compounds.

Optimization of the thermal stability of NLO chromophores ultimately requires knowledge of the decomposition mechanisms so that the appropriate structural changes can be identified and implemented. Standard thermal analytical techniques can be used to compare chromophore stability but other ancillary techniques including electrochemistry and TGA-MS can provide the required additional mechanistic insights. The full sequence and scope of the decomposition process is conveniently evaluated by thermogravimetric analysis coupled with tandem atmospheric pressure chemical ionization mass spectrometry (TGA-APCI/MS/MS) [16]. In this paper the thermal stability of three derivatives of 4-amino-4′-nitroazobenzene are investigated in which the amine donor ($R_1=R_2$) varies from diethyl to di-*n*-propyl to diphenyl. The objective is to provide mechanistic insight into the thermal decomposition of these compounds that will aid in the general development of high temperature stable NLO chromophores.

Experimental

NLO Chromophores

The three derivatives of 4-amino-4′-nitroazobenzene studied here are all known compounds. The N,N-diethyl and N,N-di-*n*-propyl substituted nitroazobenzenes were readily prepared by azo coupling of equivalent amounts of 4-nitrobenzenediazonium tetrafluoroborate (Aldrich) with N,N-diethylaniline (Aldrich) or N,N-dipropylaniline (Eastman), respectively, in a mixture of chilled acetic acid and propionic acid. These reactions are very fast and the pure dyes are obtained by simple precipitation with water, filtration and recrystallization from 1-propanol. Preparation of the N,N-diphenyl substituted nitrobenzene from the much less reactive triphenylamine required use of dichloromethane as a cosolvent, dodecylbenzenesulfonic acid as a phase transfer catalyst [17] and final silica gel chromatography and recrystallization from 1-propanol for purification.

Electrochemistry

Oxidation potentials were determined in acetonitrile solutions at a concentration of $10^{-3}M$ in chromophore and $0.10M$ in tetraethylammonium tetrafluroborate. The value E_{ox} in volts is the maximum of the oxidation wave at a sweep rate of 200 mV sec^{-1} *vs.* a standard calomel electrode.

DSC

Differential scanning calorimetry was used to provide information on the melting behavior and thermal decomposition of the NLO chromophores [9–14]. Measurements were performed on a TA Instruments 910 DSC/2100 Thermal Analyzer system. Two to four milligrams of sample were sealed in hermetic pans, after which a needle was used to make a small hole in the lid. The DSC was purged with dry nitrogen. Samples were heated at 20°C min^{-1}. The typical DSC for these azo dyes shows first an endothermic melting event (T_m) followed by a distinct exothermic decomposition event (although in some cases the decomposition does occur immediately on melting). The extrapolated onset of the decomposition exotherm (T_{di}) as well as the temperature of the exotherm maximum (T_{dm}) were taken as measures of the thermal stability, as illustrated in Fig. 1 and Table 2. As previously discussed the values of T_{di} and T_{dm} are heating rate dependent and the actual practical use temperature for a chromophore will be on the order of 50 to 100°C less than T_{di}.

Table 2 Oxidation potential and thermoanalytical characterization of NLO chromophores. Oxidation potential is the maximum of the first peak at 200 mV sec^{-1} *vs.* calomel. All thermal analysis at 20°C min^{-1}. TGA in an open pan in air; DSC in a sealed pan with pinhole in N_2

		TGA	←	DSC	→
$R_1 = R_2$	E_{ox} /V	T_5 /°C	T_m /°C	T_{di} /°C	T_{dm} /°C
Ethyl	0.99	235	156	322	335
n-propyl	0.99	234	122	331	346
Phenyl	1.09	300	140, 157*	393	412

*Two endothermic melting peaks of approximately equal ΔH_f.

TGA

Thermogravimetric analysis was used to record weight loss processes involving evaporation and degradation [9 –14]. Measurements were performed on a Perkin-Elmer TGS-2 interfaced to an Omnitherm ATvantage Contoller/Data System. The TGA was purged with dry air at 50 ml min^{-1}. Two to four milligram samples were heated in an open pan at 20°C min^{-1}. The temperature at 5% weight loss (T_5) was taken as a measure of sample volatility and/or thermal stability, as illustrated in Fig. 2 and Table 2. With TGA alone it is often not possible to distinguish between weight loss processes due to physical loss of sample *vs.* decomposition.

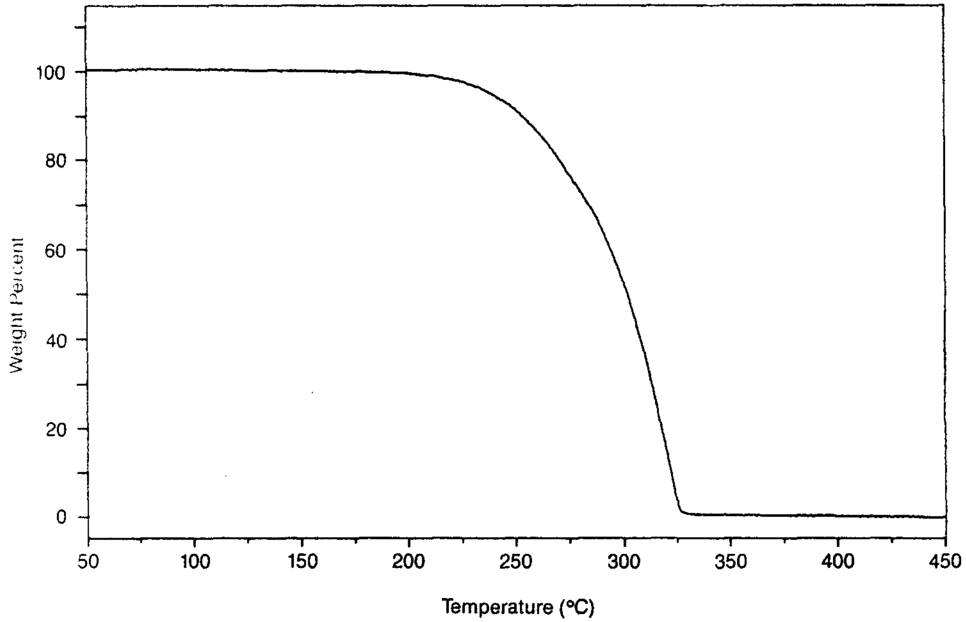


Fig. 2 TGA of 4-N, N-di-*n*-propylamino-4′-nitroazobenzene. Open pan, 20°C min^{-1} in air. T_5 =234°C

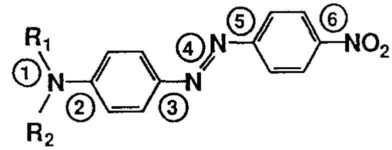
TGA/APCI-MS

Thermogravimetric analysis coupled with mass spectrometry was used to distinguish between evaporation and decomposition weight loss processes and to shed light on the mechanism of decomposition through the identification and specific evolution of major decomposition products. The TGA/mass spectrometer system used in these studies consists of a Perkin-Elmer TGS-2 thermogravimetric analyzer and a Sciex TAGA 6000 MS/MS tandem triple quadrapole mass spectrometer [16]. One to two milligram samples, sealed in a hermetic DSC pan with pinhole to suppress evaporation, were heated at 10°C min^{-1} under a 100 ml min^{-1} air purge. Approximately 10% of the TGA effluent was swept into the mass spectrometer with a 2 liter min^{-1} carrier gas for analysis. The temporal resolution between the two instruments is excellent, with less than 1 second time delay between weight loss in the TGA and mass detection in the mass spectrometer. The atmospheric pressure chemical ionization (APCI) ion source of the Sciex system permits the TGA to operate under a variety of atmospheric environments; in this study ultra-pure, dry air was used as both the TGA purge gas and the carrier gas. The systems are physically coupled by a heated, all glass transfer line. The relatively high gas velocities plus the approximately 200°C interface temperatures, including the TGA furnace tube, help to avoid condensation of less volatile materials on the interface walls.

Molecules entering the ion source from the transfer line are converted to their quasi-molecular or molecular ions, which are then focused into the high vacuum analyzer portion for standard MS or MS/MS analysis. In this study the positive ion mode was utilized, where ionization occurs by proton transfer from hydrated protons formed in the carrier gas. Those compounds whose proton affinities are greater than that of water are detected as MH^+, where M represents a volatile decomposition product of the chromophore or the intact chromophore itself. Since APCI is a soft ionization process the spectra tend to consist predominantly of molecular ions with few fragment ions.

Results and discussion

The three 4-amino-4'-nitroazobenzene derivatives studied in this work are described in Structure 1 and Tables 1 and 2. Structure 1 shows the locations of six specific bonds which are involved in the thermal degradation chemistry of these azodyes. Based on the TGA and DSC characterization data, the diethyl compound and the di-*n*-propyl compound have comparable stabilities while the diphenyl compound is considerably more stable. The fact that the 5% weight loss temperature, T_5, is so much lower than T_{di} in Table 2 suggests that evaporation may be the predominant weight loss process for TGA in open pans. As suggested by Figs 1 and 2, most of the TGA weight loss for the dipropylamino compound has occurred before the onset of decomposition by DSC (T_5=234°C,



Structure 1 Derivatives of 4-amino-4'-nitroazobenzene. The three compounds studied have $R_1 = R_2$ = Ethyl, *n*-Propyl and Phenyl. The circled numbers refer to the bonds which are involved in the degradation process

Table 3 Ion evolution data for species formed from breakage of bonds shown in structure 1, compared with data for evaporation of parent compound. TGA at 10°C min^{-1} in air, sealed pan with pinhole. T_5 = 290°C (ethyl), 270°C (*n*-propyl) and 335°C (phenyl)

B*	R = Ethyl		R = *n*-Propyl		R = Phenyl	
1	MH^+=45 Onset: 210°C Max: broad MODERATE	MH^+=271 Onset: 280°C Max: 315°C MODERATE	MH^+=59 Onset: 200°C Max: broad MODERATE	MH^+=285 Onset: 270°C Max: 305°C LOW	MH^+=95 Onset: 350°C Max: 400°C LOW	MH^+=319 Onset: 340°C Max:400°C LOW
2	MH^+=74 Onset: 250°C Max: 310°C LOW	MH^+=228 Onset: 295°C Max: 325°C LOW	MH^+=102 Onset: 265°C Max: 305°C LOW	MH^+=228 NOT DETECTED	MH^+=170 Onset: 330°C Max: 395°C HIGH	MH^+=228 NOT DETECTED
3	MH^+=150 Onset: 230°C Max: 315°C MODERATE	MH^+=150 Onset: 230°C Max: 315°C MODERATE	MH^+=178 Onset: 280°C Max: 310°C MODERATE	MH^+=150 Onset: 275°C Max: 315°C MODERATE	MH^+=246 Onset: 290°C Max:400°C LOW	MH^+=150 NOT DETECTED
4	MH^+=165 Onset: 280°C Max: 320°C HIGH	MH^+=139 Onset: 275°C Max: 315°C HIGH	MH^+=193 Onset: 275°C Max: 310°C MODERATE	MH^+=139 Onset: 270°C Max: 310°C HIGH	MH^+=261 Onset: 290°C Max:400°C LOW	MH^+=139 Onset: 305°C Max: 400°C HIGH
5	MH^+=177 Onset: 290°C Max: 315°C LOW	MH^+=122 Onset: 290°C Max: 315°C HIGH	MH^+=205 Onset: 280°C Max: 310°C LOW	MH^+=122 Onset: 265°C Max: 310°C HIGH	MH^+=273 NOT DETECTED	MH^+=122 Onset: 305°C Max: 390°C HIGH
6	MH^+=254 Onset: 280°C Max: 320°C LOW	NO POSITIVE ION	MH^+=282 Onset: 250°C Max: 310°C LOW	NO POSITIVE ION	MH^+=350 Onset: 340°C Max: 400°C LOW	NO POSITIVE ION
P*	MH^+=299 Onset: 150°C	HIGH Max: 290°C	MH^+=327 Onset: 160°C	HIGH Max: 300°C	MH^+=395 Onset: 190°C	HIGH Max: 330°C

B* Bond broken (Structure 1); P* Parent compound:
Note: Relative abundance of ions listed as LOW, MODERATE or HIGH.

temperature at full weight loss is 325 and T_{di}=331°C). T_5 measured in a sealed pan with pinhole, as reported in Table 3, is considerably higher even when measured at a slower heating rate; furthermore, TGA conducted in this manner results in a residue or char consisting of 50 to 70% of the original weight. Of the three compounds studied only the diphenyl would have adequate thermal stability, as measured by T_{di}, to be considered a candidate NLO chromophore for electro-optical applications.

Figure 3 is a mass spectrum obtained at the maximum rate of weight loss during TGA/MS of 4-N,N-diethylamino-4′-nitroazobenzene, where the maximum weight loss rate is coincidental with the maximum ion evolution. Several

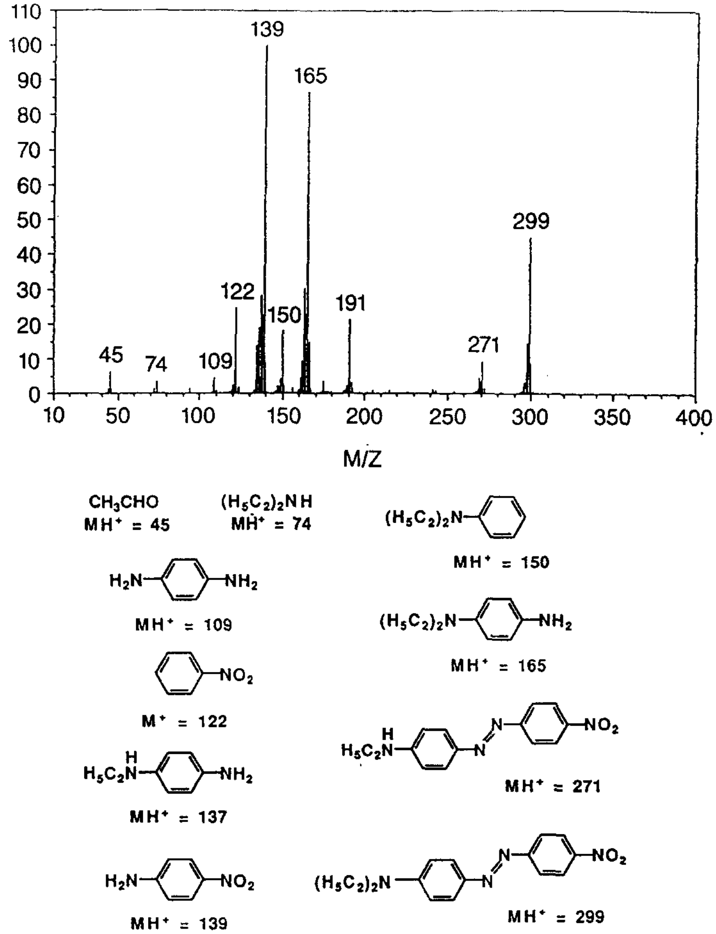


Fig. 3 Average of positive ion APCI-MS spectra of 4-N, N-diethylamino-4′-nitroazobenzene obtained between 300 and 340°C (maximum rate of weight loss). All data normalized to m/z = 139 intensity. Identification of parent compound and major decomposition products are shown

of the evolved species are identified below the mass spectrum. They include *p*-nitroaniline ($MH^+ = 139$) and 4-N,N-diethylamino-4′-aminobenzene ($MH^+ = 165$) as major decomposition products, suggesting that the azo (–N–N–) bond (bond 4 in Structure 1) is highly susceptible to cleavage. The large abundance of the parent compound ($MH^+ = 299$) is evidence that evaporation competes effectively with decomposition. Note in Table 3 that all three species show high relative abundances based on integrated ion intensities. The evolution of 4-N-ethylamino-4′-nitroazobenzene ($MH^+ = 271$) is evidence for dealkylation (involving cleavage of bond 1 in Structure 1). Decomposition involving a dealkylation mechanism has also been observed in bulk pyrolysis experiments, e.g., 4-N-ethylamino-4′-nitroazobenzene is produced along with numerous other byproducts upon heating 4-N,N-diethylamino-4′-nitroazobenzene to 260°C. The presence of acetaldehyde ($MH^+ = 45$) coupled with the absence of ethyl radicals is evidence for an oxidative dealkylation process. As shown in Table 3 acetaldehyde is the earliest decomposition product to evolve (at 210°C). The 4-N-ethylamino-4′-nitroazobenzene fragment is undoubtedly also produced at this lower temperature but probably may not be sufficiently volatile or stable to appear with significant intensity. Note in Fig. 3 that the abundance of 4-amino-4’-nitroazobenzene ($MH^+ = 243$) is low, suggesting that loss of two ethyl groups to form the fully hydrogen substituted chromophore ($R_1 = R_2 = H$) is not a significant reaction (or another reaction, such as azo bond cleavage, intervenes). The identification of $M^+ = 122$ as the radical cation of nitrobenzene formed from cleavage of Bond 5 in Structure 1 is supported by the fragmentation of similar nitro-substituted azobenzenes in electron impact mass spectrometry [17, 20].

Figure 4 is a mass spectrum obtained at the maximum rate of weight loss during TGA/MS of 4-N,N-di-*n*-propylamino-4′-nitroazobenzene. Evolved species for this dipropyl substituted dye which were not observed for the diethyl substituted dye are identified below the mass spectrum in Fig. 4. The weight loss process is entirely analogous to that of the diethyl compound. Major decomposition products are *p*-nitroaniline ($MH^+ = 139$) and 4-N,N-di-*n*-propylamino-4′-aminobenzene ($MH^+ = 193$), suggesting again that the azo bond (bond 4) is readily cleaved. The large abundance of the parent compound ($MH^+ = 327$) again demonstrates that weight loss occurs by evaporation as well as decomposition. In fact, the di-*n*-propyl compound seems to be somewhat more volatile than the diethyl compound in spite of its higher molecular weight. The presence of propionaldehyde coupled with the absence of propyl radicals further supports oxidative dealkylation as the most facile decomposition pathway. As shown in Table 3, propionaldehyde is first detected at 200°C, 50 to 100°C below the onset of the evolution of other decomposition products. In particular, the 4-N-*n*-propylamino-4′-nitroazobenzene fragment ($MH^+ = 285$) from dealkylation is not seen until 270°C, again perhaps due to its much lower volatility. Once again complete dealkylation to form 4-amino-4′-nitroazobenzene ($MH^+ = 243$) is evidently not a significant degradation process.

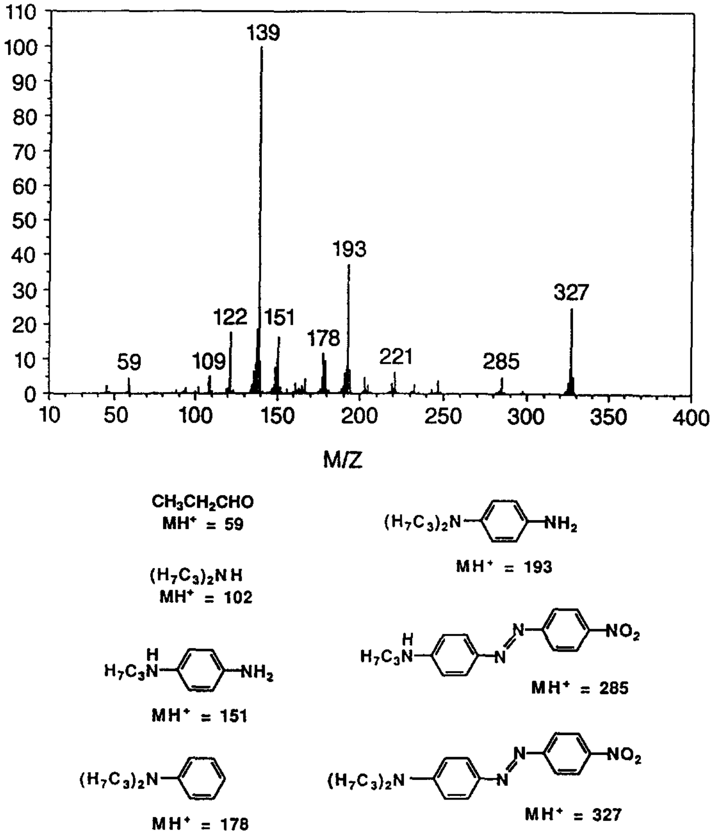


Fig. 4 Average of positive ion APCI-MS spectra of 4-N, N-di-*n*-propylamino-4′-nitroazobenzene obtained between 300 and 340°C (maximum rate of weight loss). All data normalized to $m/z = 139$ intensity. Identification of parent compound and major decomposition products are shown

Figure 5 shows ion evolution profiles for selected species illustrating the dealkylation process beginning at about 200°C ($MH^+=59$), evaporation of the parent compound starting just below 200°C ($MH^+=327$), evolution of a major decomposition product ($MH^+=139$) starting at about 270°C and reaching maximum evolution near 315°C, and evolution of a late decomposition product starting at about 295°C and reaching maximum evolution close to 330°C ($MH^+=109$). We believe that there is one broad evolution of propionaldehyde but that this species or an isomer behaves as a reagent ion between 300 and 330°C, giving rise to the shape of the reconstructed ion thermogram for $MH^+=59$. The source of the 1,4-diaminobenzene ($MH^+=109$) is uncertain; it certainly arises from a sequence of events involving scission of the azo bond and may come from the nitro fragment by subsequent reduction and/or the diethylamine fragment via dealkylation.

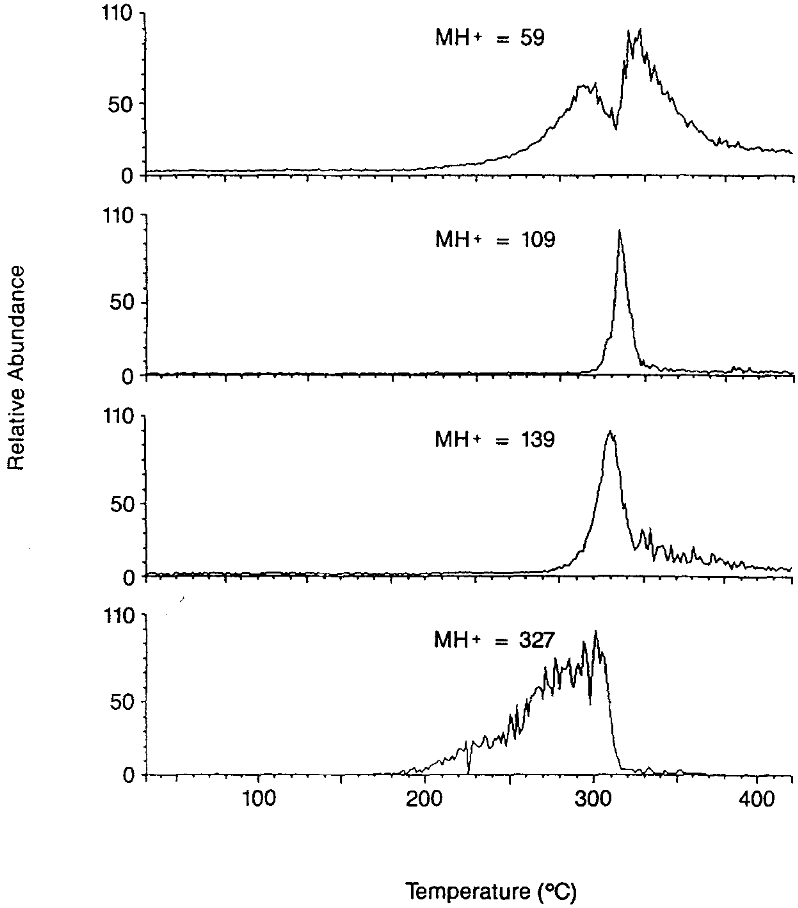


Fig. 5 Reconstructed ion DSC curves of 4-N, N-di-*n*-propylamino-4'-nitroazobenzene during thermogravimetric analysis in sealed pan with pinhole, demonstrating simultaneous decomposition and evaporation/sublimation

Figure 6 is a mass spectrum obtained for 4-N,N-diphenylamino-4'-nitroazobenzene at the maximum rate of weight loss. The decomposition pathway is quite different for this diarylamine donor compound compared to the dialkylamine compounds just discussed. First, there is just an overall smaller number of evolved species as compared to the decomposition of the diethyl and di-*n*-propyl compounds. The major products evolved are identified below the mass spectrum and include *p*-nitroaniline ($H^+=139$) and diphenylamine ($MH^+=170$). The large abundance of the parent compound ($MH^+=395$) demonstrates that evaporation and decomposition compete effectively. The fact that the diphenyl compound is lost by evaporation to such a large extent in spite of the fact it has the highest molecular weight attests to its enhanced thermal stability. A process analogous to the oxidative dealkylation observed in the diethyl and

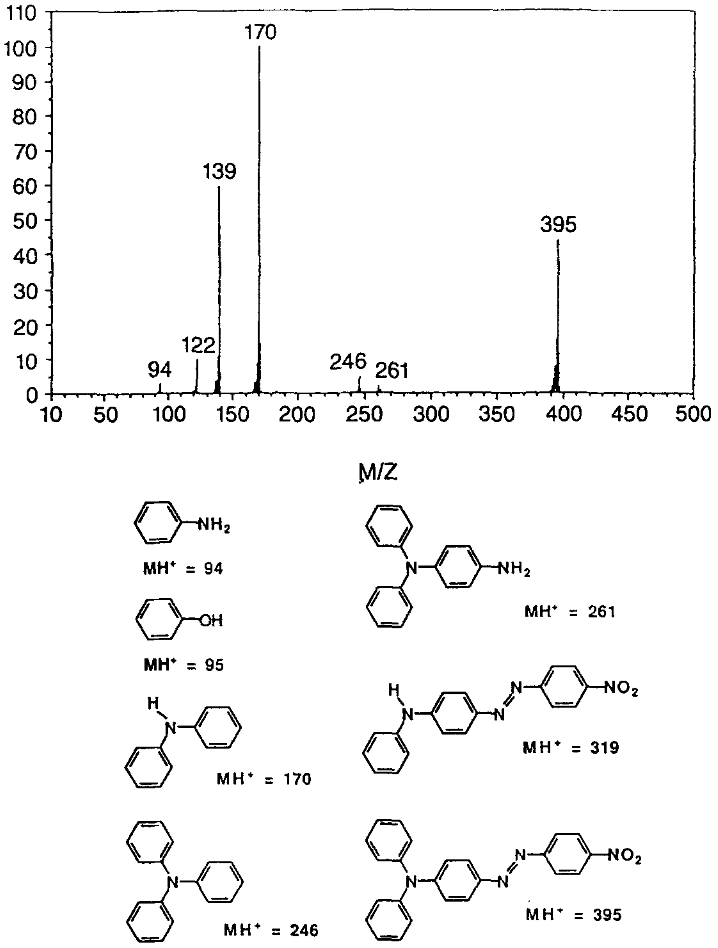


Fig. 6 Average of positive ion APCI-MS spectra of 4-N, N-diphenylamino-4′-nitroazobenzene obtained between 380 and 420°C (maximum rate of weight loss). All data normalized to m/z = 170 intensity. Identification of parent compound and major decomposition products are shown

di-*n*-propyl compounds would be expected to produce 4-N-phenylamino-4′-nitroazobenzene ($MH^+ = 139$) and phenol ($MH^+ = 95$). However, the dephenylated product is not observed at all and an ion corresponding to the molecular weight of protonated phenol was detected but at very low levels. Instead of monodephenylation (breakage of bond 1) the entire diphenylamine unit ($MH^+ = 170$ due to breakage of bond 2) is now a predominant decomposition fragment. Simple cleavage of the azo bond as occurred extensively in the diethyl and di-*n*-propyl compounds would be expected to form *p*-nitroaniline and 4-N,N-diphenylamino-4′-aminobenzene ($MH^+ = 261$); the latter is observed but at relatively low abundance. Figure 7 shows ion evolution profiles for selected

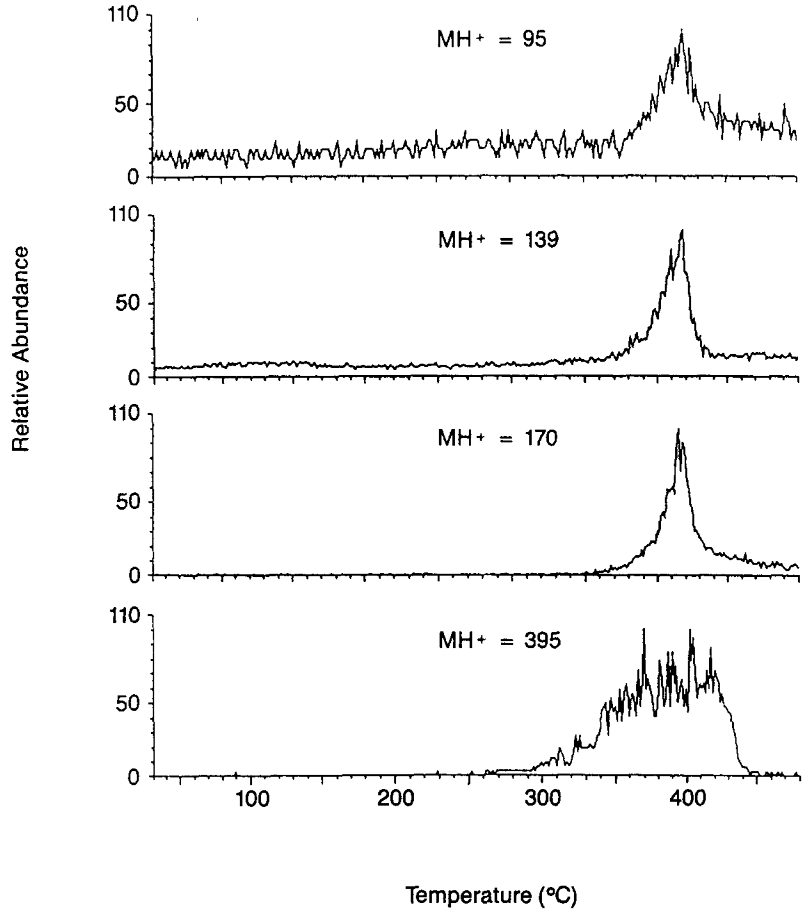


Fig. 7 Reconstructed ion thermograms of 4-N, N-diphenylamino-4'-nitroazobenzene during thermogravimetric analysis in sealed pan with pinhole

species illustrating the evaporation of the parent compound starting just below 300°C ($MH^+=395$) and the uniform evolution of three decomposition products ($MH^+=95$, 139 and 170).

As indicated in Table 3, amongst the three azobenzene derivatives studied evidence was detected for the breakage of all bonds in Structure 1. In the decomposition spectra of all three compounds *p*-nitroaniline and the radical cation of nitrobenzene exhibit consistently high abundances. Common to the decomposition spectra of all compounds studied were decomposition products corresponding to the protonated species Parent – 149, i.e. $MH^+=150$, 178 and 246 for the diethyl, dipropyl and diphenyl compounds, respectively. Similar ions were observed as fragment ions in the electron impact mass spectra of a series of azobenzenes [21], and correspond to the breakage of Bond 3 in Structure 1.

The thermal stabilities of the diethyl and di-*n*-propyl derivatives of 4-amino-4′-nitroazobenzene are very similar. In both compounds decomposition begins near 200°C at 10°C min^{-1} by oxidative dealkylation of one of the nitrogen alkyl substituents. The thermal decomposition pathways found for these compounds share much in common with the electrochemical decomposition pathways proposed by Fasani *et al.* for this class of azodyes [22]. In the electrochemical degradation it is proposed that an electron is removed from the molecule at the anode to first give a radical cation. This radical cation then subsequently decomposes by two pathways involving either dealkylation on nitrogen or cleavage at the azo linkage. In the thermal degradation the nitro group is the chemical oxidant and itself is reduced (probably to species such as a nitroso group of hydroxylamine which are themselves unstable to the reaction conditions and are not isolated or detected). The similarities in products obtained from the electrochemical and thermal processes are striking.

The thermal stability of 4-N,N-diphenylamino-4′-nitroazobenzene is markedly higher, with the onset of decomposition occurring at ~100°C higher temperature than in the dialkyl compounds. As described in Table 3 and Fig. 7 and in contrast to the decomposition of the dialkyl compounds, the onset of decomposition is accompanied by the simultaneous evolution of several decomposition products. As also shown in Table 3 some corresponding products observed in the decomposition of the dialkyl compounds were not observed in the decomposition of the diphenyl compounds. These decomposition products appear to be associated with bonds 3 and 5 in Structure 1.

For all three derivatives of 4-amino-4′-nitroazobenzene studied weight loss by evaporation of the parent compound competed effectively with decomposition. Thus significant increases in thermal stability could have the adverse effect of simply shifting the process responsible for the stability of electro-optic activity from decomposition of the chromophore to its evaporation during processing or possibly its sublimation at the 80°C operating temperature.

In an earlier report [13] several general observations were made that also apply to this work:

1. The propensity for thermal decomposition appears related to the number and accessibility of α-hydrogens on the amine donor (Table 1). Compounds with methyl substituted amines are the least stable while compounds with longer N-alkyl groups or branched N-alkyl groups offer some enhancement in stability (steric effect). In the presence of a nitro group (or other acceptor group which is an oxidant) an alkylamine donor is often the most thermally labile site as alkyl groups on the donor nitrogen are lost via an oxidative thermal process. One otherwise surprising outcome was that the parent hydrogen substituted chromophores are more stable than most of their alkylated derivatives. This is due to both an increase in oxidation potential as the alkyl groups on nitrogen are

replaced by hydrogen and just a simple statistical reduction in the number of labile α-hydrogens on the alkyl groups as these alkyl groups are replaced by hydrogen.

2. Substitution of aryl groups for alkyl groups leads to significantly enhanced stability. A single aryl group on the nitrogen donor is not nearly as effective as are two aryl groups. The aryl groups enhance stability at least in part simply due to the fact that they do not possess any reactive α-hydrogen atoms.

3. The stability within a series is related to the oxidation potential. Structural changes and additional substituents which raise the oxidation potential tend to enhance the thermal stability (and vice-versa). Substituents have varying influence as a function of their identity, number and location. For example, branched alkyl groups may influence the accessibility of the α-hydrogen and in aryl substituted amines additional groups on the aromatic ring will influence the oxidation potential. Substitution of aryl groups for alkyl groups leads to enhanced stability in part due to the overall increase of the oxidation potential which results upon this substitution.

Conclusions

The optimization of the thermal stability of NLO chromophores ultimately requires knowledge of the decomposition mechanisms so that structural fixes can be implemented. Standard thermal analytical techniques can be used to compare relative chromophore stabilities but other supplementary techniques including cyclic voltammetry and TGA/MS provide the requisite additional mechanistic insights.

The oxidative thermal degradation processes of derivatives of 4-amino-4′-nitroazobenzene were investigated by DSC, TGA and TGA/MS. For 4-N,N-diethylamino-4′-nitroazobenzene and 4-N,N-di-*n*-propylamino-4′-nitroazobenzene the onset of decomposition involves abstraction of an α-hydrogen, oxidation of the resulting carbon radical and the ultimate elimination of the alkyl group as the respective aldehyde. This process appears to commence even at temperatures of about 200°C based on detection of the aldehyde byproducts. At 50 to 100°C higher temperatures the onset of other degradation processes involving other bonds are observed. For 4-N,N-diphenylamino-4′-nitroazobenzene the amine alkyl group reaction mechanism is not available and comparable fragmentation of phenyl groups appears not to contribute to degradation. For example, no benzene and only minor amounts of phenol were observed. Instead, in the 330 to 350°C range (10°C min^{-1}) the onset of fragmentation of other bonds (such as the aryl-azo and azobenzene-diphenylamine bonds) is observed. Evaporation was observed to compete effectively with decomposition of all three compounds studied, suggesting the ultimate necessity of attaching the chromophore directly to the host polymer backbone. Further fine tuning of these structures by appropriate introduction of substituents is anticipated to provide some further enhancement in thermal stability. It is important to note that substitution of the aryl substituents for alkyl on the amine donor enhances thermal stability with little or no compromise in nonlinearity [14]. Evaluation of the scope of the utility of this aryl donor substitution on other types of chromophores which contain other combinations of π-conjugation and acceptor groups is underway.

* * *

The authors acknowledge contributions by colleagues at IBM including H. Truong and R. Siemens for the thermal analysis. This work was supported by the Air Force Office of Scientific Research and the National Institute of Science and Technology Advanced Technology Program.

References

1 J. Zyss, Ed., 'Molecular Nonlinear Optics. Materials, Physics, Devices' Academic Press, San Diego 1994.
2 D. Burland, R. D. Miller and C. Walsh, Chem. Rev., 94 (1994) 31.
3 R. Lytel, G. F. Lipscomb, E. S. Binkley, J. T. Kenny and A. J. Ticknor, Proc. SPIE, 1215 (1990) 252.
4 W. E. Moerner and S. Silence, Chem. Rev., 94 (1994) 127.
5 C. A. Walsh, D. M. Burland, V. Y. Lee, R. D. Miller, B. Smith, R. J. Twieg and W. Volksen, Macromol., 26 (1993) 3720.
6 J. W. Wu, J. F. Valley, S. Ermer, E. S. Binkley, J. T. Kenney, G. F. Lipscomb and R. Lytel, Appl. Phys. Lett., 58 (1991) 225.
7 B. Zysset, M. Ahlheim, M. Staehelin, F. Lehr, P. Pretre, P. Kaatz and P. Günter, Proc. SPIE, 2025 (1993) 70.
8 E. Muller, Ed., Methoden der Organishen Chemie, IV/1b, Oxidation Teil 2, 1975 pp. 967–985.
9 R. J. Twieg, K. M. Betterton, D. M. Burland, V. Y. Lee, R. D. Miller, C. R. Moylan, W. Volksen and C. A. Walsh, Proc. SPIE, 2025 (1993) 94.
10 R. D. Miller, K. M. Betterton, D. M. Burland, V. Y. Lee, C. R. Moyland, C. A. Walsh and W. Volksen, Proc. SPIE, 2042 (1994) 354.
11 R. J. Twieg, D. M. Burland, J. L. Hedrick, V. Y. Lee, R. D. Miller, C. R. Moylan, W. Volksen and C. A. Walsh, Mater. Res. Soc. Symp. Proc., 328, L. R. Dalton, Ed., 1994 p. 421.
12 R. J. Twieg, D. M. Burland, J. Hedrick, V. Y. Lee, R. D. Miller, C. R. Moylan, C. M. Seymour, W. Volksen and C. A. Walsh, Proc. SPIE, 2143 (1994) 2.
13 R. Twieg, V. Lee, R. D. Miller, C. Moylan, R. B. Prime and G. Chiou, Polym. Prepr., 35(2) (1994) 200.
14 C. R. Moylan, R. J. Twieg, V. Y. Lee, S. A. Swanson, K. M. Betterton and R. D. Miller, J. Amer. Chem. Soc., 115 (1994) 12599.
15 G. Hallas, J. Soc. Dyers, Colour., 95 (1979) 285.
16 R. B. Prime and B. Shushan, Anal. Chem., 61 (1989) 1195.
17 M. Ellwood and J. Griffiths, J. C. S. Chem. Comm., (1990) 181.
18 J. H. Bowie, G. E. Lewis and R. G. Cooks, J. Chem. Soc. (B), (1967), 621.
19 Yu. S. Nekrasov, V. A. Puchkov and N. S. Vul'fson, J. Gen. Chem. USSR, 38 (1975) 1337.
20 H. P. Mehta and A. T. Peters, Appl. Spec., 28(3) (1974) 241.
21 J. A. Vollmin, P. Pachlatko and W. Simon, Helv. Chim. Acta, 52 (1969) 47.
22 E. Fasani, T. Soldi, A. Albini and S. Pietra, Gazz. Chim. Ital., 120 (1990) 109.