# Optical Limiting Properties of [60]Fullerene Derivatives

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Optical limiting properties of methano[60]fullerene and pyrrolidino[60]fullerene derivatives in room-temperature solutions are studied systematically. The results show that the derivatives are very similar to the parent [60]fullerene in optical limiting, despite the fact that the linear absorption and emission properties of the derivatives are very different from those of [60]fullerene. The optical limiting properties of the [60]fullerene derivatives are discussed in the context of nonlinear optical effects due to reverse saturable absorption.

## Introduction

Materials exhibiting significant nonlinear optical effects have attracted much recent attention.[1] In particular, organic dyes that are strong nonlinear absorbers are being investigated as optical limiting materials for potential applications in the protection of sensors and human eyes from intense laser radiations.[1,2] An ideal optical limiter should have linear transmittance at low incident light fluences and become opaque at high light levels. The materials under investigation include metallophthalocyanines,[2−5] diphenylpolyenes and polyacene-based compounds,[6,7] mixed metal clusters,[8−10] and fullerenes.[11] For the laser radiation at 532 nm fullerenes, especially [60]fullerene ($C_{60}$), are among the best of all materials in optical limiting properties.[11] In addition, $C_{60}$-based materials may be considered as potent broadband optical limiters due to the broad coverage of the characteristic ground- and excited-state absorptions over a wide wavelength range.

Several approaches have been developed for the fabrication of fullerenes into optical limiting devices.[12−18] For example, optical limiting properties of $C_{60}$ dispersed in a poly(methyl methacrylate) (PMMA) matrix have been investigated.[17] Technical difficulties in the material processing include poor solubilities of fullerene molecules in common organic solvents and insolubilities in polar solvents. Thus, fullerene derivatives with better solubility characteristics are more desirable. In fact, $C_{60}$ derivatives have been used in the preparation of fullerene-containing glasses by use of sol−gel techniques.[15] A broader limiting bandwidth was achieved by incorporating $C_{60}$ and a second optical limiting material in the same sol−gel composites.[13] Pendant $C_{60}$ polymers have also been synthesized for the preparation of fullerene-containing polymer films for optical limiting investigations.[19] However, while fullerene derivatives may be advantageous in properties such as improved solubilities in common organic solvents, an important issue is the effect of derivatizations of fullerene cages on the optical limiting properties. A systematic examination of different fullerene derivatives for their nonlinear absorption efficiencies in comparison with the parent $C_{60}$ is necessary. Here we report a study of optical limiting properties of methano- and pyrrolidino-$C_{60}$ derivatives, which represent two important classes of functionalized $C_{60}$ compounds. The results show that the optical limiting efficiencies of the $C_{60}$ derivatives are very similar to that of the parent $C_{60}$, despite the fact that the linear absorption and emission properties of the derivatives are very different from those of $C_{60}$. The optical limiting properties of the $C_{60}$ derivatives are discussed in terms of the reverse saturable absorption mechanism developed for the parent $C_{60}$.

## Experimental Section

**Materials.** $C_{60}$ was obtained from Southern Chemical Group (purity >99.5%). The sample purity was checked by UV/vis absorption, ^{13}C NMR, and matrix-assisted laser des-

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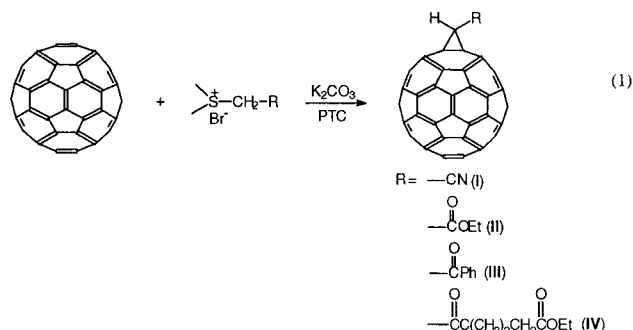
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orption ionization time-of-flight MS methods, and the sample was used without further purification. Spectrophotometric grade toluene, chloroform, and methanol were obtained from Burdick & Jackson and used as received. $CS_2$ was obtained from Baker and distilled before use.

Methano-$C_{60}$ derivatives **I**−**IV** were prepared by use of the reactions of $C_{60}$ with stabilized sulfonium ylides with cyano, carboxy, and carbonyl groups.[20] The one-pot preparation was carried out under phase transfer conditions. A toluene solution of $C_{60}$, sulfonium salts, $K_2CO_3$, and the phase transfer catalyst tetrabutylammonium bromide (TBAB) were mixed and reacted at room temperature. The stabilized sulfonium ylides generated *in situ* due to the deprotonation of the sulfonium salts by $K_2CO_3$ under the catalysis of TBAB undergo nucleophilic addition to $C_{60}$, followed by intramolecular substitution to form methano-$C_{60}$ derivatives with the simultaneous elimination of dimethyl sulfide.



$$R = \quad -CN \text{ (I)}$$

$$-\overset{O}{\overset{\|}{C}}OEt \text{ (II)}$$

$$-\overset{O}{\overset{\|}{C}}Ph \text{ (III)}$$

$$-\overset{O}{\overset{\|}{C}}C(CH_3)_2CH_2\overset{O}{\overset{\|}{C}}OEt \text{ (IV)}$$

In a typical one-pot reaction, 100 mg (0.14 mmol) of $C_{60}$ in 60 mL of anhydrous toluene, 0.16 mmol of sulfonium bromide, 200 mg of anhydrous $K_2CO_3$, and 20 mg of the catalyst TBAB were added to a 100 mL round-bottom flask. After purging with dry nitrogen gas, the flask was sealed, and the reaction mixture was stirred at room temperature for 24 h. The mixture was then filtered to remove any solids and concentrated by evaporation under vacuum. Results from the matrix-assisted laser desorption ionization time-of-flight MS analysis show the presence of mono-, bis-, and tris-adducts. The mono-adduct was obtained after separation from higher order adducts through silica gel column chromatography using $CS_2$ as an eluent. The methano-$C_{60}$ derivatives are brown solids and more soluble than $C_{60}$ in common organic solvents such as chloroform. The yields for the preparations of the methano-$C_{60}$ derivatives **I**−**IV** are in the range 42−53%.

Proton and $^{13}C$ NMR results clearly demonstrate the [6,6] ring junction for the methylene bridge. It is interesting that, in contrast to the preparation of methano-$C_{60}$ based on addition reactions of diazo compounds,[21] no isomers with [6,5] ring junction were found in the reaction mixtures of the sulfonium ylide addition.

The pyrrolidino-$C_{60}$ derivative *N*-ethyl-*trans*-2′,5′-dimethylpyrrolidino[3′,4′:1,2]-$C_{60}$ (**V**) was obtained from photochemical reactions of $C_{60}$ and triethylamine. The purification and structural characterization of the compound have been reported elsewhere.[22]



(V)
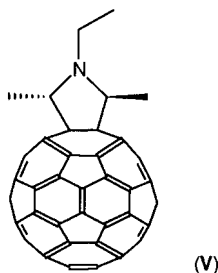
**Measurements.** UV/vis absorption spectra were obtained using a computer-controlled Shimadzu UV2101-PC spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped
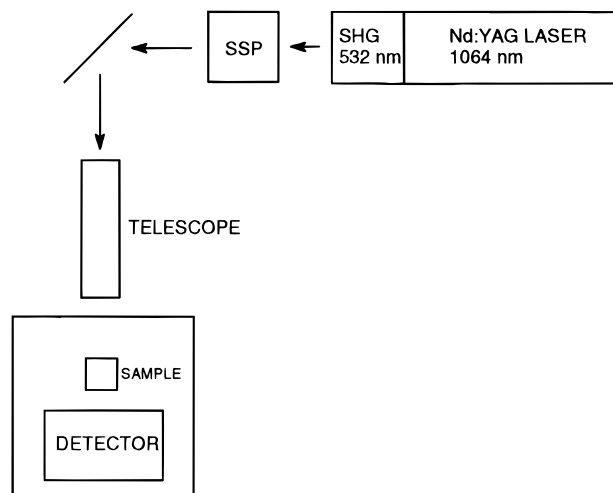


**Figure 1.** Experimental setup for optical limiting measurements.

with a 450 W xenon lamp, a Spex 340S dual-grating and dual-exit monochromator, and two detectors. The two gratings are blazed at 500 nm (1200 grooves/mm) and 1000 nm (600 grooves/mm). The room-temperature detector consists of a Hamamatsu R928 photomultiplier tube operated at 950 V, and the thermoelectronically cooled detector consists of a near-infrared-sensitive Hamamatsu R5108 photomultiplier tube operated at 1500 V. A Schott 540 nm (GG-540) or 610 nm (RG-610) color glass sharp-cut filter was placed before the emission monochromator to eliminate the excitation scattering. Unless specified otherwise, fluorescence spectra were corrected for nonlinear instrumental reponse by use of predetermined correction factors. The correction factors for the emission spectrometer were carefully determined by using a calibrated radiation standard obtained from Optronic Laboratories.[23]

Optical limiting measurements were performed by use of a setup illustrated in Figure 1. It consists of a Continuum Surelite-I Q-switched Nd:YAG laser as the light source, which can be operated from a single shot to 10 Hz. The infrared fundamental was frequency-doubled to generate the second harmonic at 532 nm. It was isolated by use of a Surelite harmonic separation package. The maximum energy at 532 nm is 160 mJ/pulse with a 5 ns pulse width (fwhm). The last output was varied in a range 5−160 mJ/pulse by adjusting the delay time of the Q-switch from its optimal setting. The laser beam has a diameter of 6 mm, corresponding to energy densities 0.02−0.6 J/cm². A Galilean style telescope consisting of a plano-concave lens, and a plano-convex lens was used to reduce the laser beam waist to 3 mm in diameter for higher energy densities up to 2.25 J/cm². A Molectron PM10V1 volume absorbing probe coupled with a PM500A meter was used as the detector. For measurements in the single shot mode, a Scientech Mentor MC2501 calorimeter and a MD10 meter were employed. Solution samples were measured in a cuvette with 2 mm optical path length.

## Results and Discussion

**Linear Absorption and Emission.** The methano- and pyrrolidino-$C_{60}$ derivatives have very different UV/vis absorption spectra from that of the parent $C_{60}$ (Figure 2). A characteristic feature in the observed UV/vis absorption spectra of the $C_{60}$ derivatives is a weak band at ∼700 nm, with molar absorptivities of 250−300 $M^{-1}$ $cm^{-1}$. While the spectra of different methano-

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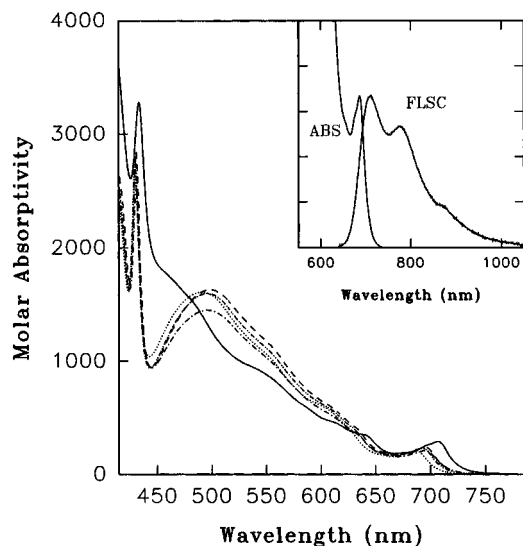(23) Ma, B.; Sun, Y.-P. *J. Chem. Soc., Perkin Trans. 2* 1996, 2157.

**Figure 2.** Absorption spectra of methano-$C_{60}$ (**I**, -··-; **II**, -···-; **III**, - - -; **IV**, ···) and pyrrolidino-$C_{60}$ (—) derivatives in room-temperature toluene. The fluorescence spectrum of **I** is shown in the inset.

$C_{60}$ derivatives are rather similar among themselves, they are somewhat different from the spectrum of the pyrrolidino-$C_{60}$ derivative. At 532 nm, molar absorptivities of the methano-$C_{60}$ derivatives **I**−**IV** are in the range 1180−1340 $M^{-1}$ $cm^{-1}$, and the molar absorptivity of the pyrrolidino-$C_{60}$ derivative **V** is 970 $M^{-1}$ $cm^{-1}$, which is only slightly larger than that of the parent $C_{60}$ (940 $M^{-1}$ $cm^{-1}$).[24] The observed absorbances are proportional to the solution concentrations of the $C_{60}$ derivatives, obeying Lambert−Beer's law.

The fluorescence spectra of the derivatives are also different from that of $C_{60}$. Shown in Figure 2 is the spectrum of the methano-$C_{60}$ cyanide derivative (**I**). The spectra of other derivatives are similar.

**Optical Limiting.** The optical limiting properties of the $C_{60}$ derivatives were measured by use of the setup shown in Figure 1. For the methano-$C_{60}$ cyanide derivative (**I**), optical limiting measurements were carried out in toluene solutions with linear transmittances of 55 and 70% at 532 nm. Both solutions show significant optical limiting at moderate input light fluences ($I_{IN}$) (Figure 3). The optical limiting threshold, which is defined as the input light fluence at which the output light fluence ($I_{OUT}$) is 50% of what is predicted by the linear transmittance, is 0.22 $J/cm^2$ for the solution with linear transmittance of 55% and 0.31 $J/cm^2$ for the solution with linear transmittance of 70%. At higher input fluences, $I_{OUT}$ reaches a plateau, with the saturated $I_{OUT}$ value of 0.056 and 0.110 $J/cm^2$ for the solutions of 55 and 70% linear transmittances, respectively (Figure 3). The results for other methano-$C_{60}$ derivatives are quite similar. As shown in Figure 4, toluene solutions of the methano-$C_{60}$ benzoyl derivative also exhibit significant optical limiting at moderate $I_{IN}$ values. A comparison of the optical limiting threshold and saturated $I_{OUT}$ values for different methano-$C_{60}$ derivatives in toluene solutions is given in Table 1.

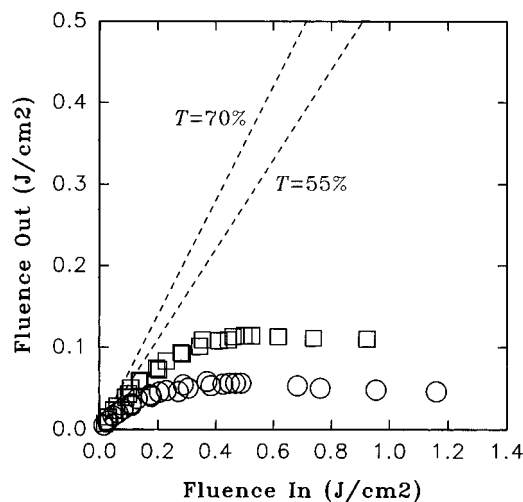For comparison, toluene solutions of the parent $C_{60}$ with linear transmittances of 55, 65, 70, and 82% were

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**Figure 3.** Optical limiting results of the methano-$C_{60}$ cyanide derivative (**I**) in toluene solutions with linear transmittances of 55% (○) and 70% (□).
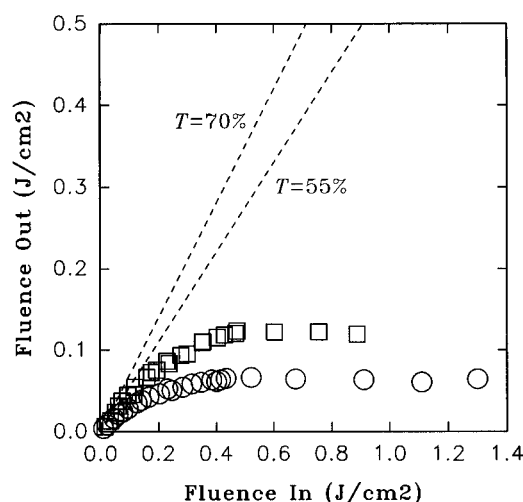


**Figure 4.** Optical limiting results of the methano-$C_{60}$ benzoyl derivative (**III**) in toluene solutions with linear transmittances of 55% (○) and 70% (□).

**Table 1. Optical Limiting Properties of the $C_{60}$ Derivatives**

| | | limiting threshold $(J/cm^2)^a$ | | $I_{OUT}$ at saturation $(J/cm^2)$ | |
|---|---|---|---|---|---|
| sample | solvent | $T = 55\%$ | $T = 70\%$ | $T = 55\%$ | $T = 70\%$ |
| **I** | toluene | 0.22 | 0.31 | 0.056 | 0.11 |
| **II** | toluene | 0.25 | 0.30 | 0.06 | 0.1 |
| **II** | dichlorobenzene | 0.25 | 0.34 | 0.07 | 0.12 |
| **II** | chloroform | 0.22 | 0.33 | 0.06 | 0.12 |
| **III** | toluene | 0.25 | 0.35 | 0.06 | 0.12 |
| **IV** | toluene | 0.21 | 0.31 | 0.06 | 0.11 |
| $C_{60}$ | toluene | 0.18 | 0.31 | 0.05 | 0.1 |
| $C_{60}$ | toluene ($T = 65\%$) | 0.2 | | 0.06 | |
| $C_{60}$ | toluene ($T = 82\%$) | 0.45 | | 0.18 | |
| **V** | toluene ($T = 65\%$) | 0.22 | | 0.07 | |
| **V** | toluene ($T = 82\%$) | 0.48 | | 0.19 | |

$^a$ The optical limiting threshold is defined as the input light fluence at which the output light fluence is 50% of what is predicted by the linear transmittance.

measured by use of the setup shown in Figure 1 under the same experimental conditions. The results at 65 and 82% linear transmittances agree well with those reported by Tutt and Kost.[11] As shown in Table 1, the optical limiting threshold and saturated $I_{OUT}$ values of the parent $C_{60}$ and methano-$C_{60}$ derivatives are rather
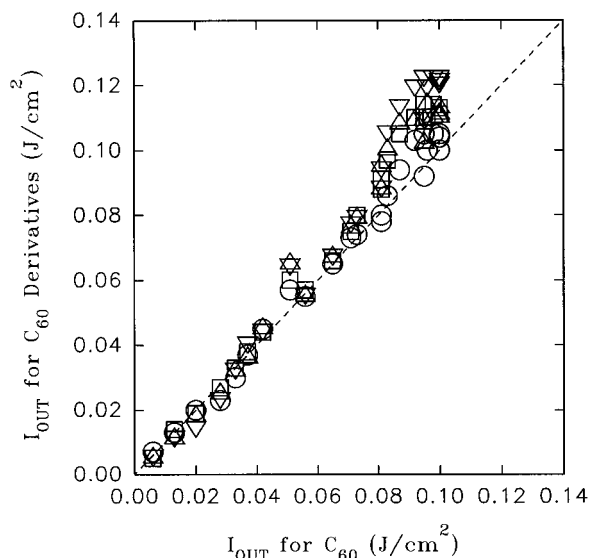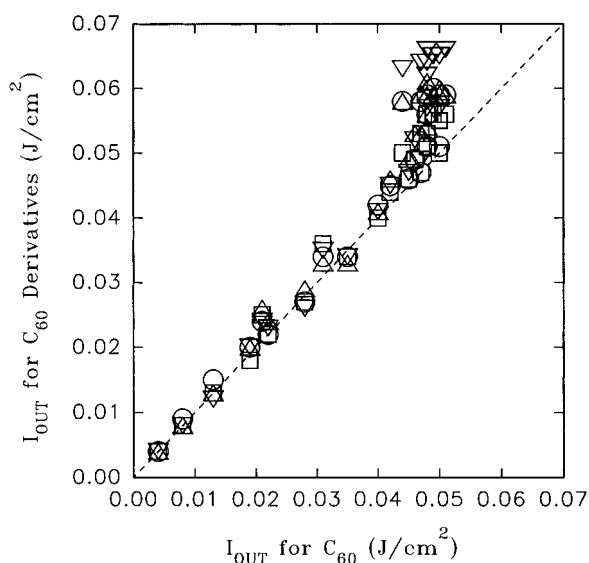
**Figure 5.** Plot of the output light fluences for the methano-$C_{60}$ derivatives vs $C_{60}$ at the same input light fluences and the same linear transmittances of 70% (**I**, □; **II**, ○; **III**, ▽; **IV**, △).



**Figure 6.** Plot of the output light fluences for the methano-$C_{60}$ derivatives vs $C_{60}$ at the same input light fluences and the same linear transmittances of 55% (**I**, □; **II**, ○; **III**, ▽; **IV**, △).

similar. In Figures 5 and 6 the optical limiting results of the methano-$C_{60}$ derivatives are compared with those of the parent $C_{60}$ by plotting the $I_{OUT}$ values for the derivatives vs the $I_{OUT}$ values for the parent $C_{60}$ at the same $I_{IN}$ values. The plots are close to linear with slopes near unity, indicating that the dependencies of nonlinear absorptions on $I_{IN}$ in the methano-$C_{60}$ derivatives and in the parent $C_{60}$ are essentially the same.

The optical limiting properties of ethyl methano-$C_{60}$ carboxylate (**II**) were examined in different solvents at linear transmittances of 55 and 70%. As shown in Figure 7 and Table 1, the optical limiting results for ethyl methano-$C_{60}$ carboxylate in toluene, o-dichlorobenzene, and chloroform are essentially the same.

There is also significant optical limiting in toluene solutions of the pyrrolidino-$C_{60}$ derivative (**V**). At linear transmittances of 65 and 82%, the observed optical limiting thresholds are 0.22 and 0.48 J/cm², respectively. The saturated $I_{OUT}$ values at the plateau are 0.07 J/cm² for 65% linear transmittance and 0.190 J/cm² for 82%
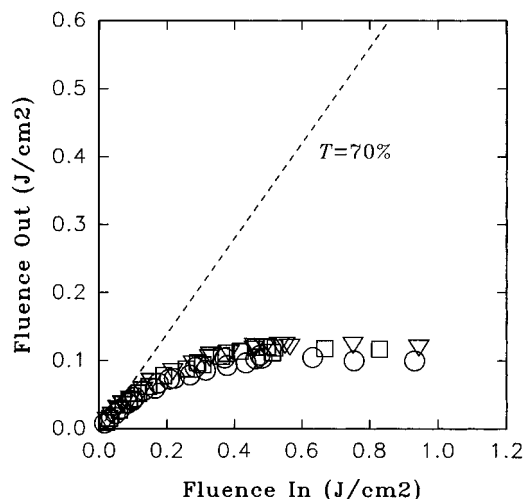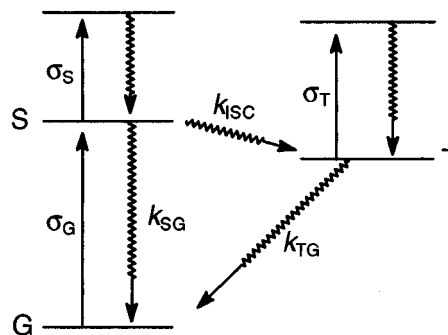


**Figure 7.** Optical limiting results of the methano-$C_{60}$ ester derivative (**II**) in toluene (○), o-dichlorobenzene (□), and chloroform (▽) solutions with a linear transmittance of 55%.

**Scheme 1**



linear transmittance. The results are again similar to those of the parent $C_{60}$ (Table 1).

The optical limiting properties of $C_{60}$ have been explained in terms of a reverse saturable absorption mechanism.[25] The reverse saturable absorption in organic dyes and fullerenes can be described by a five-level model (Scheme 1). As the incident light transmits through the sample with a path length of $L$, the photon flux $i$ (photons cm$^{-2}$ s$^{-1}$) changes with the distance $x$ in a nonlinear fashion due to significant excited-state absorptions.

$$\mathrm{d}i/\mathrm{d}x = -\sigma_G N_G i - \sigma_S N_S i - \sigma_T N_T i \qquad (2)$$

where $\sigma$ denotes absorption cross sections (cm²) and the subscripts (G, S, and T) indicate the corresponding electronic states as shown in Scheme 1. $N$ represents the molecular populations in the different states, which are time-dependent. By assuming that the populations in the upper excited states are negligible,

$$\mathrm{d}N_S/\mathrm{d}t = \sigma_G N_G i - (k_{SG} + k_{ISC})N_S \qquad (3)$$

$$\mathrm{d}N_T/\mathrm{d}t = k_{ISC}N_S - k_{TG}N_T \qquad (4)$$

An expression for $N_G$ is not necessary because of the relationship $N_G = N - (N_S + N_T)$, where $N$ is the total molecular population. Reverse saturable absorption occurs when the excited-state cross sections are larger

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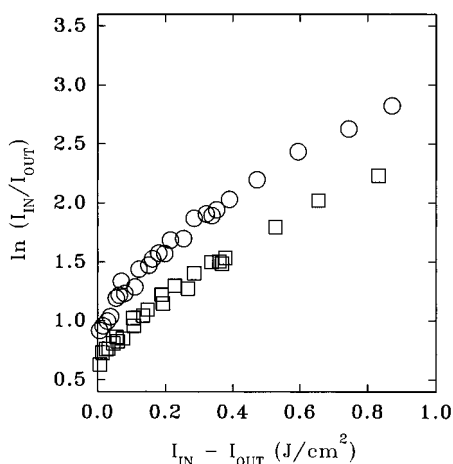
**Figure 8.** Treatment based on eq 6 for the optical limiting results, of the methano-$C_{60}$ cyanide derivative (**I**) in toluene solutions with linear transmittances of 55% (○) and 70% (□).

than the ground-state cross section, $\sigma_{EFF}/\sigma_G > 1$, where $\sigma_{EFF}$ includes a weighted average of $\sigma_S$ and $\sigma_T$.[2] This is certainly the case for $C_{60}$, with $\sigma_S$ ($1.6 \times 10^{-17}$ cm$^2$) and $\sigma_T$ ($9.5 \times 10^{-18}$ cm$^2$) both significantly larger than $\sigma_G$ ($3.1 \times 10^{-18}$ cm$^2$) at 532 nm.[25] For the methano- and pyrrolidino-$C_{60}$ derivatives, the $\sigma_G$ values are similar to that of the parent $C_{60}$. The transient absorption spectra of the methano- and pyrrolidino-$C_{60}$ derivatives are not available. However, flash photolysis studies of a methano-$C_{60}$ derivative with a [6,6] ring junction[26] and a pyrrolidino-$C_{60}$ derivative[27] show that the triplet−triplet absorption spectra are similar to the spectrum of $C_{60}$. It seems logical to expect that the excited-state absorptions of the $C_{60}$ derivatives considered here are also similar to those of the parent $C_{60}$. Thus, the optical limiting properties of the $C_{60}$ derivatives may also be attributed to nonlinear effects as a result of reverse saturable absorption.

The application of the five-level model for reverse saturable absorption is essentially a problem of solving the differential equations (2)−(4). For the optical limiting properties of $C_{60}$ in a toluene solution, McLean et al. have used numerical integrations to solve the differential equations of the five-level model for reverse saturable absorption (Scheme 1).[25] The results of modeling show that the optical limiting of $C_{60}$ at 532 nm follows the five-level model with incident light fluences up to ∼1 J/cm$^2$ for 8 ns pulsed laser and higher for a 30 ps pulsed laser.[25] Similar treatments for the derivatives are not possible due to a lack of some

fundamental parameters such as excited-state absorption cross sections. However, because of the excellent correlations between the optical limiting results of the $C_{60}$ derivatives and the parent $C_{60}$ (Figures 5 and 6), it is expected that the nonlinear absorptions in the $C_{60}$ derivatives should also follow the five-level reverse saturable absorption model.

In the treatment of optical limiting results of polyacene-based oligomers in terms of the five-level model, Kojima et al. introduced quasi-steady-state approximations for $N_S$ and $N_T$.[7] Therefore, eq 2 can be solved analytically to yield the expression as follows.[7]

$$\ln(I_{IN}/I_{OUT}) = b \ln[(1 + aI_{IN})/(1 + aI_{OUT})] + c \quad (5)$$

where $a$ and $b$ are functions of the decay rate constants and absorption cross sections and are independent of $I_{IN}$ and $I_{OUT}$, and $c = \sigma_G NL$. By assuming $aI_{IN}$ and $aI_{OUT}$ much smaller than 1, eq 5 can be further simplified in Maclaurin expansions,[7]

$$\ln(I_{IN}/I_{OUT}) = ab(I_{IN} - I_{OUT}) + c \quad (6)$$

Thus, a linear relationship between $\ln(I_{IN}/I_{OUT})$ and $(I_{IN} - I_{OUT})$ may be expected according to eq 6. Such plots for the optical limiting results of the $C_{60}$ derivatives are not linear. For example, the results for the methano-$C_{60}$ derivative **II** in toluene solutions with linear transmittances of 70 and 55% are shown in Figure 8. The plots are curved, with the curvature more significant in the plot for 55% linear transmittance. Similar deviations from linearity were observed in the treatment of the optical limiting results of polyacene-based oligomers.[7] The deviations were attributed to the approximate nature of eq 6. However, a closer examination of the assumptions used for the derivation of eqs 5 and 6 reveals that the quasi-steady-state approximation for the excited triplet-state population $N_T$ is the most problematic. Because the triplet-state relaxation times $1/k_{TG}$ of $C_{60}$ and derivatives are on the order of 100 $\mu$s, the predominating process during the 5−10 ns laser pulse is the buildup of the excited triplet state. As a result, eqs 2−4 may not be simplified with quasi-steady-state approximations.

While the $C_{60}$ derivatives are equally potent optical limiters as the parent $C_{60}$, the derivatives have improved solubility characteristics. Their solubilities in common organic solvents make them better candidates in the fabrication of optical limiting devices. Preparations and measurements of polymer thin films containing the $C_{60}$ derivatives for potential optical limiting applications are in progress.

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