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Laser-Induced Carbene−Carbene Rearrangement in Solution: The Diphenylcarbene−Fluorene Rearrangement

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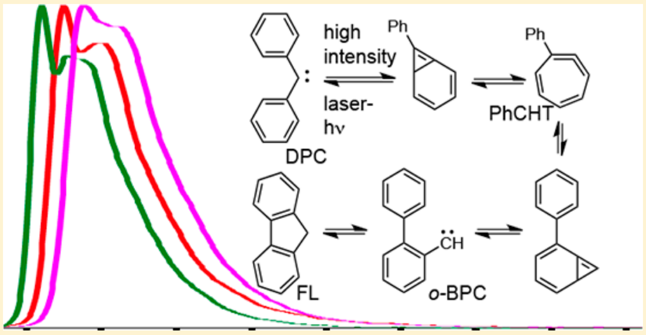
Ⓢ Supporting Information



ABSTRACT: Diphenylcarbene (DPC) generated by high-intensity laser photolysis of diphenyldiazomethane rearranges to fluorene (FL) by two distinct mechanisms as revealed by methyl-group labeling. Thus, excimer laser irradiation of *p,p′*-dimethyldiphenyldiazomethane generates 3,6-dimethylfluorene (3,6-DMF) and 2,7-dimethylfluorene (2,7-DMF), which were identified by fluorescence measurements as well as GC-MS and comparison with authentic materials. 3,6-DMF corresponds to direct bond formation between *ortho* positions in DPC, referred to as *ortho,ortho′* coupling. 2,7-DMF corresponds to a carbene−carbene rearrangement, whereby DPC undergoes ring expansion to phenylcycloheptatetraene (PhCHT) followed by ring contraction to *o*-biphenylylcarbene (*o*-BPC), which then cyclizes to FL. The carbene−carbene rearrangement dominates over the *ortho,ortho′* coupling under all conditions employed. The *ortho,ortho′* coupling must take place in a higher excited state (most likely S_2 or T_1) of DPC, because it is not observed at all under thermolysis conditions, where only S_1 and T_0 are populated. The carbene−carbene rearrangement may take place either in a hot S_1 state or more likely in a higher excited state (S_2 or T_1).

INTRODUCTION

In 1980, Turro and co-workers reported the rearrangement of diphenylcarbene (DPC), **2**, to fluorene, **3**, in the high-intensity excimer laser photolysis of diphenyldiazomethane (DPDM), **1**. (Scheme 1).[1] In addition, tetraphenylethene (TPE), **4**, diphenylphenanthrene (DPP), **5**, and diphenylanthracene (DPA), **6**, were also formed.

While TPE is a "normal" carbene reaction product, formed by dimerization of the ground state T_0 carbene,[2] fluorene (**3**), DPP (**5**), and DPA (**6**) have never been observed in conventional UV lamp photolysis of **1**, where benzophenone azine (BPA) and TPE are major products (Scheme 2).[2,3] It is known that photolysis of TPE followed by air oxidation can lead to DPP formation,[4] but this is apparently not the major source of DPP in the excimer laser photolysis. Under high-intensity photolysis conditions, a relatively high concentration of diphenylcarbene (DPC), **2**, is obtained, thus making multiphoton chemistry and intertransient reactions possible,[2] here leading to FL, DPP, and DPA.

DPC has a triplet ground state, T_0, which has been well characterized by ESR, UV (absorption and emission), and IR spectroscopy.[5] Experiments and calculations indicate that the first excited singlet state, S_1, lies ca. 3 kcal/mol above T_0.[6,7] The small energy gap causes fast $S_1 \rightarrow T_0$ conversion in fluid solution ($k \approx 10^{10}$ s^{-1}), and the reverse $T_0 \rightarrow S_1$ reaction is ca. 3 orders of magnitude slower.[6] The S−T conversion is solvent dependent: a polar solvent such as acetonitrile stabilizes the singlet, probably by ylide formation. This leads to a smaller S−T gap and slower intersystem crossing of S_1 to T_0.[8] Thus, the S_1 lifetime is ∼120 ps in cyclohexane and ∼340 ps in acetonitrile.[8,9] The S_1 singlet state is formed from DPDM within 30 ps of a 266 nm laser pump pulse and decays to T_0 in 300 fs.[10,11] S_1 and T_0 have UV absorption maxima at ∼370 and 320 nm, respectively.[11,12] The excited T_1 state of DPC absorbs at ca. 360 nm in CH_3CN, fluoresces at ∼500 nm,[13] and decays to the ground state triplet, T_0, on a time scale of 4−9 ns in hydrocarbon solution[6,13] or 30−140 ns time scale in an ethanol glass at 77 K.[14] The T_1 state is formed under the high-intensity laser conditions used by Turro and co-workers, who observed its emission at 507 nm.[1]

The formation of fluorene (FL), **3**, under conditions of high photon density has been proposed to occur via the exited states S_1[1,2,15] or T_1.[16] Turro and co-workers[1] stated that the formation of FL is dependent on the laser intensity and suggested that it might be produced from S_1. Wilson and Schnapp proposed further excitation of S_1 to a higher excited singlet state, presumably S_2. This is referred to as ^{1}DPC* in Scheme 3. It was suggested that this state might have a π-system similar to the diphenylmethyl cation and undergo photochemical cyclization to **7** followed by hydrogen migration to give FL, **3** (Scheme 3, route a).[2] However, FL was not produced under the laser-jet photolysis conditions used by these authors.[2,6]

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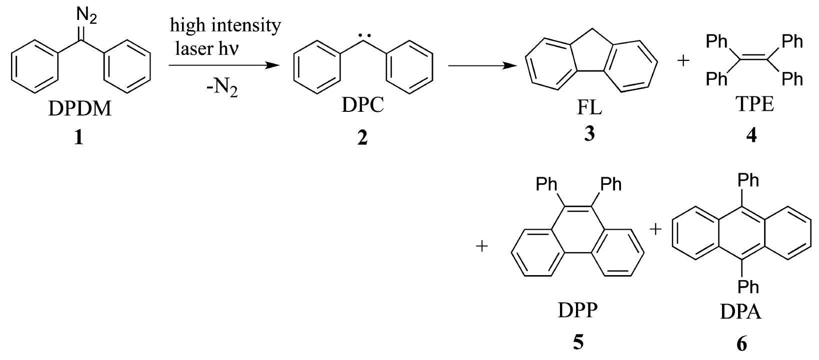
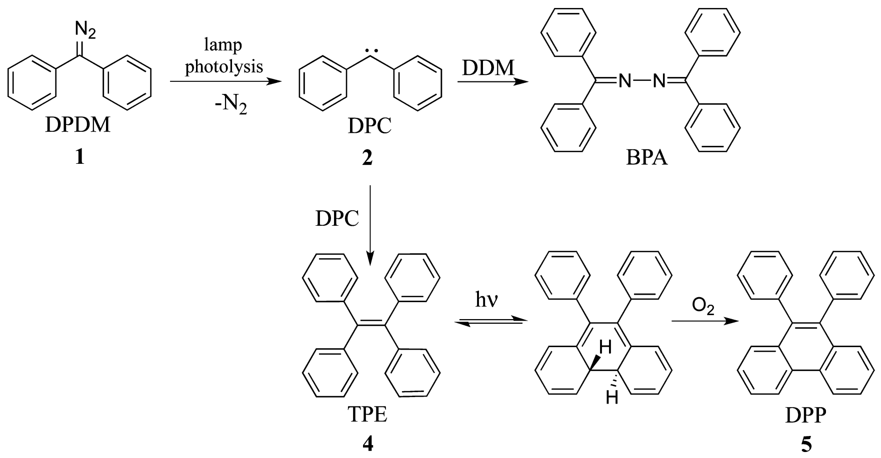
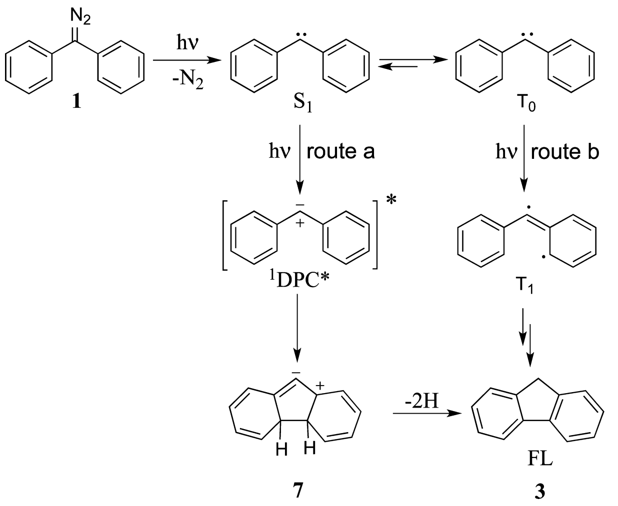
Scheme 1. Products of High-Intensity Laser Photolysis of DPDM



Scheme 2. Products of Conventional Photolysis of DPDM



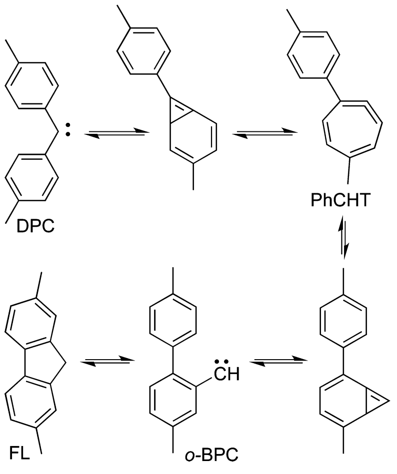
Scheme 3. Two Proposed Mechanisms for *ortho,ortho′*-Coupling in Diphenylcarbene



Despres et al. proposed another mechanism (Scheme 3, route b) whereby the first excited triplet state, T_1, was held responsible for the production of FL, DPP, and DPA.[16] In particular, it was expected that FL, **3**, was formed by the *ortho,ortho′* bond formation (Scheme 3).

Both of the proposed mechanisms for the formation of FL in Scheme 3 involve bond formation between the *ortho,ortho′* positions of DPC. Quite a different mechanism has been established for the *thermal* isomerization of DPC to FL, which takes place in the gas phase under flash vacuum thermolysis (FVT) conditions (Scheme 4). Here, it is well established that the reaction proceeds via carbene–carbene rearrangement through ring expansion to phenylcycloheptatetraene (PhCHT) and ring contraction to *o*-biphenylylcarbene (*o*-BPC). An *ortho,ortho′* bond formation is not involved at all.[17]

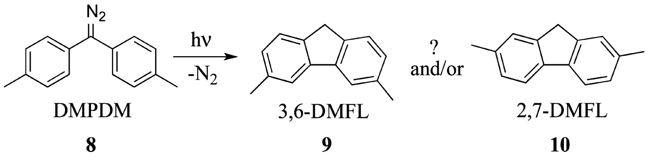
Scheme 4. The Carbene–Carbene Mechanism for Fluorene Formation from Diphenylcarbene under FVT Conditions



Therefore, in order to determine whether the carbene–carbene rearrangement is involved in the laser-induced reaction, we have investigated the photolysis of *p,p′*-dimethyldiphenyldiazomethane (DMPDM), **8** (Scheme 5). The direct *ortho,ortho′*-coupling would produce 3,6-dimethylfluorene

(3,6-DMFL), **9**, whereas the carbene−carbene rearrangement would produce 2,7-dimethylfluorene (2,7-DMFL), **10**.

Scheme 5



■ RESULTS

The laser-drop (LD) photolysis technique[18] has proven very valuable for preparative multiphoton laser photochemistry. It has the advantage of directing the laser pulse to a single drop of solution, favoring multiphoton chemistry to take place. Laser excitation of the hanging drop of solution causes it to burst into smaller droplets that are splattered onto the walls of the photolysis cell. The photolyzed drop is then collected in the bottom part of the cell, out of the path of the next laser pulse directed at the new drop that is forming. Therefore, we used this technique in the photolyses of diphenyldiazomethanes with 308 and 248 nm pulsed excimer lasers delivering 75−90 and 75−180 mJ pulses, respectively.

A concentration of 5×10^{-5} M of DPDM in hexane was used for the laser-drop experiments, since dilution will favor the unimolecular process(es) responsible for fluorene formation. Figure 1 gives the emission spectrum of a photolyzate recorded using an excitation wavelength of 250 nm. The spectrum is in good agreement with the report by Turro et al.[1] and dominated by an emission band arising from fluorene with maxima at 305 and 315 nm. This was confirmed by comparison with the emission spectrum obtained for an authentic sample of FL in hexane (Figure 2a).

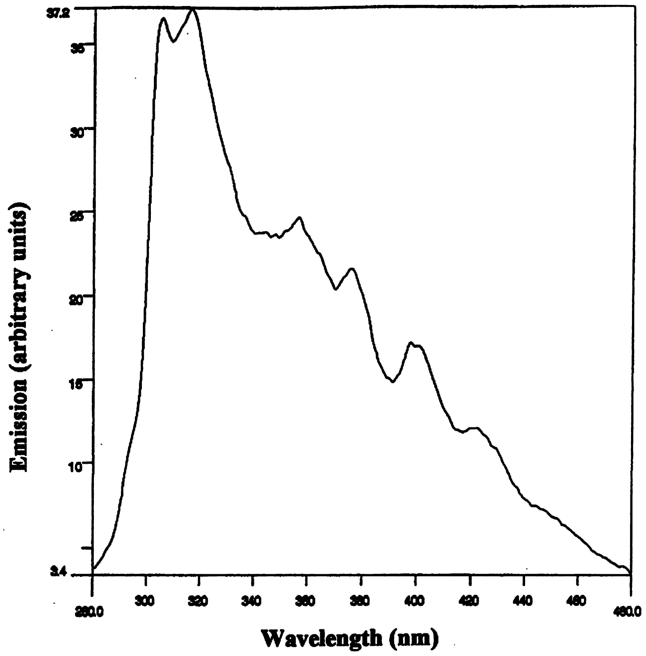


Figure 1. Emission spectrum (λ_{exc} = 250 nm) after laser-drop photolysis of a 5×10^{-5} M solution of DPDM in hexane at 308 nm (90 mJ/pulse).

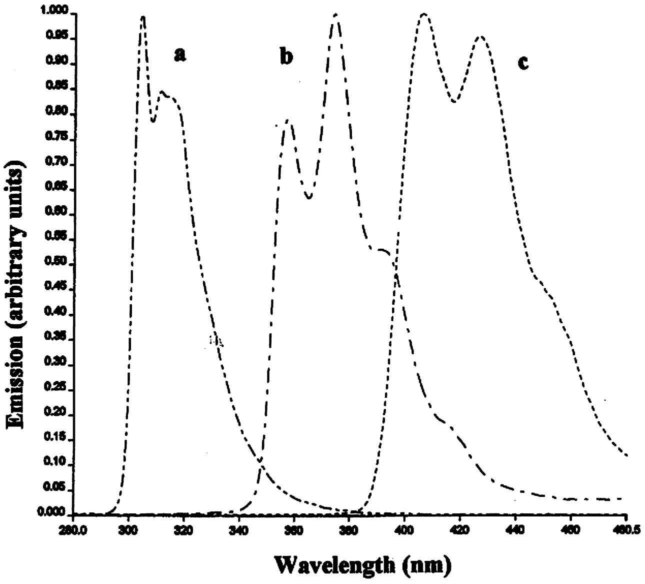


Figure 2. Emission spectrum (λ_{exc} = 250 nm) of hexane solutions of (a) fluorene (FL), (b) 9,10-diphenylphenanthrene (DPP), and (c) 9,10-diphenylanthracene (DPA).

Poorly resolved emission bands with maxima at 355, 375, 395, and 420 nm are also observed in Figure 1. These are due to 9,10-diphenylphenanthrene (DPP), **5**, and 9,10-diphenylanthracene (DPA), **6**.[1] Figure 2b,c gives the emission spectra of authentic samples of DPP and DPA in hexane for comparison.

A second cycle of LD irradiation did not result in an increase in the fluorene emission. Moreover, green emission corresponding to the relaxation of T_1 to T_0 of DPC was only observed during the first cycle of LD photolysis. Accordingly, one cycle of LD photolysis was deemed sufficient to decompose all of the diphenyldiazomethane.

As mentioned above, the first excited state of DPC (S_1) is longer-lived in polar solvents (∼340 ps in CH_3CN) than in hydrocarbon solvents (∼120 ps in cyclohexane).[6,8] A laser-drop photolysis of DDM in CH_3CN (5×10^{-5} M) revealed that fluorene was no longer a major product. In fact, shoulders at 305 and 315 nm suggest that only a trace of FL was formed (See Figure S1, Supporting Information). A reversible formation of an acetonitrile−diphenylcarbene ylide may be responsible.[6] The enhanced stabilization of the singlet state of DPC not only slows intersystem crossing but may also allow vibrational deactivation before any chemical reactions can take place.

A preparative scale laser-drop photolysis of DPDM was carried out in order to make fluorene detectable by GC-MS. For this, 7.8 mg of **1** in 750 mL of hexane was photolyzed, and the resulting mixture was purified by preparative TLC using hexane as the eluent. Fluorescence analysis was used to identify the extracts containing fluorene. GC-MS analysis of the fluorene fraction confirmed the presence of FL by direct comparison with an authentic sample.

Hexane solutions of DPDM (5×10^{-5} M or 10^{-1} M) were also photolyzed at 254 nm using a low-pressure mercury lamp for 90, 110, 135, or 180 min. The concentrated photolysis mixtures were then purified by microcolumn chromatography prior to emission analysis. As shown in Figure S2, Supporting Information, although there is emission in the 300−320 nm region of the spectra, the characteristic band shape of FL is not obvious. If any fluorene was formed, it was only a trace amount.

Laser-Drop Photolysis of *p,p′*-Dimethyldiphenyldiazomethane (DMPDM). Having determined the necessary conditions to obtain detectable amounts of FL, it was necessary to be able to distinguish between the two possible dimethylfluorene isomers: 3,6-DMFL (**9**) and 2,7-DMFL (**10**). As shown in Figure S3, Supporting Information, the emission spectra of authentic samples of thee compounds as well as FL are very similar, although they are slightly shifted with respect to one another.

However, it was possible to distinguish between 3,6-DMFL and 2,7-DMFL by gas chromatography on either a BP21 (poly(ethylene glycol) phase, 50 m) column or a BP10 (14% cyanopropylphenyl siloxane, 86% dimethyl siloxane phase, 50 m) column, with 3,6-DMFL eluting before 2,7-DMFL in both cases. Both isomers had the same intensity response. A laser-drop photolysis of DMPDM, **8**, on a small scale demonstrated dimethylfluorene formation. A green emission was again observed, indicating that the T_1 state of *p,p′*-dimethyldiphenylcarbene was formed. The fluorescence of this first excited triplet state is known to peak at 517 nm in acetonitrile.[19] The spectrum of the photolyzate had an emission band in the 310−320 nm region, which is compatible with a mixture of 3,6-DMFL and 2,7-DMFL (Figure 3 and Figure S4, Supporting Information), although fluorescence measurements do not permit an evaluation of the amounts of the two fluorenes.

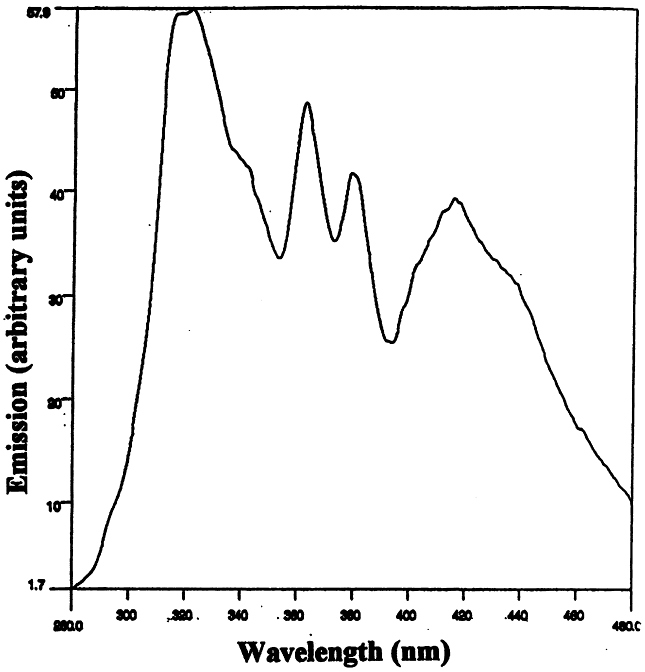
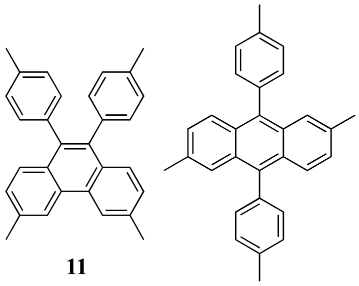


Figure 3. Emission spectrum (λ_{exc} = 250 nm) obtained after laser-drop photolysis of a 5 × 10^{-5} M solution of DMPDM in hexane at 308 nm (90 mJ/pulse).

Other emission bands present at 360, 380, and 415 nm in Figure 3 are ascribed to phenanthrene and anthracene derivatives **11** and **12** (Chart 1) analogous to the photoproducts DPP and DPA in Figure 1, but these compounds were not investigated further.

Preparative scale laser-drop experiments on DMPDM were performed as above using the two different lasers, and each photolysis mixture was purified as described above. The emission spectra of the products clearly showed that fluorenes were obtained (Figure S5, Supporting Information).

Chart 1



11

12

GC-MS analyses revealed that a mixture of both dimethylfluorene isomers was obtained in all experiments (Table 1 and Figure 4). A ratio of 1:15 for 3,6-DMFL vs 2,7-DMFL was obtained at 308 nm, and 1:8.5 or 1:6.5 at 248 nm. It appears that higher energy causes formation of relatively more 3,6-DMF.

Table 1. Fluorenes Formed in High-Intensity Laser-Drop Photolyses of *p,p′*-Dimethyldiphenyldiazomethane in Hexane (5 × 10^{-5} M)

laser wavelength (nm)	energy (mJ/pulse)	ratio[a] of 3,6-DMFL/2,7-DMFL
308	85−90	1:15
248	85−95	1:8.5
248	75−180	1:6.5

[a] Ratios are based on integrated peak areas of GC traces obtained with the BP21 capillary column.

Co-injections of authentic samples of 3,6-DMFL and 2,7-DMFL confirmed the assignments and did not result in the appearance of new peaks in the GC traces. This was confirmed on the two different GC columns (Figure 4).

Control LD photolysis experiments at 248 nm confirmed that there was no photochemical interconversion of 2,7-DMFL and 3,6-DMFL.

■ DISCUSSION

The C_7H_7 energy surface connecting phenylcarbene, cyclohepta-1,2,4,6-tetraene, and other isomers has been the subject of extensive calculations.[20] Very similar calculated activation barriers were found at the B3LYP, G2(MP2), CCSD(T), and CASPT2N levels of theory.[20] The energies of the corresponding species on the energy surface for the diphenylcarbene rearrangement at the BLYP level indicate that the highest energy barrier, TS4, lies only ca. 23 kcal/mol above the singlet DPC, **2** (S_1) (Scheme 6). This is similar to the barriers calculated for the ring expansion of phenylcarbene itself and other substituted phenylcarbenes.[21] The formation of fluorene, **3**, of course, is highly exothermic, by 75 kcal/mol. Nevertheless, fluorene formation has never been observed in solution thermolysis because other, faster bimolecular reactions take place. The carbene−carbene rearrangement to fluorene takes place only in the low-pressure flash vacuum thermolysis, where bimolecular reactions are disfavored. The cyclization of *o*-biphenylylcarbene to fluorene involves addition to the benzene ring to give 8a*H*-fluorene, followed by a H-shift.[22]

The calculations in Scheme 6 pertain to the lowest singlet state of DPC, S_1. We do not know that the same path is

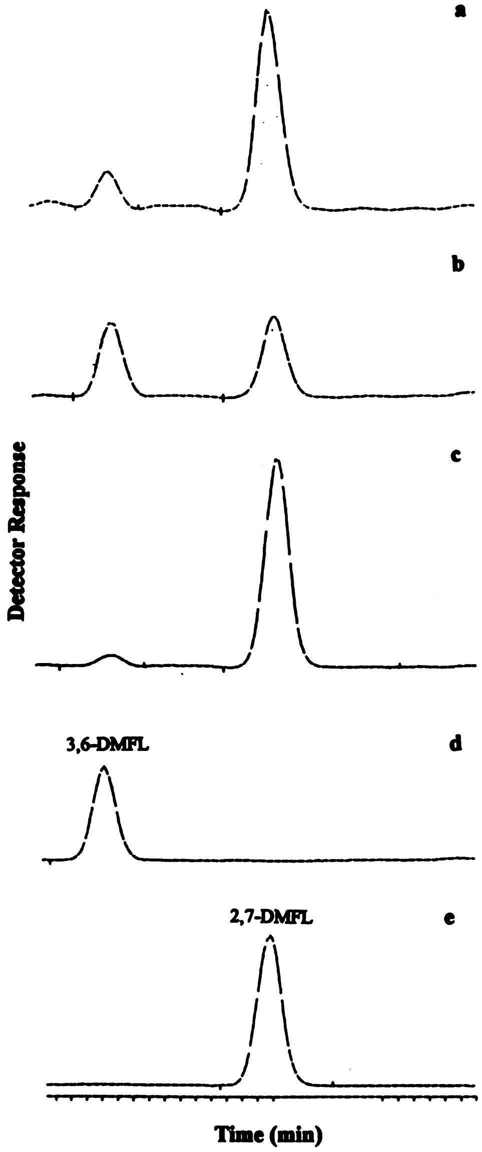
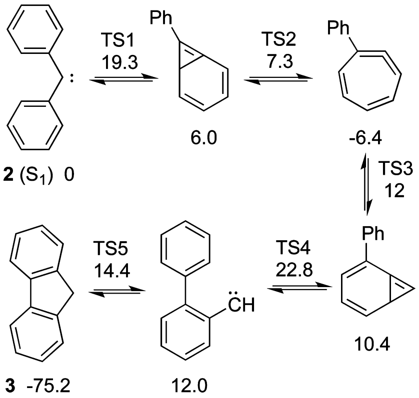


Figure 4. GC traces (BP21 column) for the laser-drop photolysis of DMPDM at 248 nm (75−180 mJ/pulse). (a) Purified photolysis mixture after laser-drop photolysis of a 5 × 10^{-5} M solution of DMDPD in hexane at 248 nm (75−180 mJ/pulse); (b) co-injection of photolysis mixture with 3,6-DMFL; (c) co-injection of photolysis mixture with 2,7-DMFL; (d) pure 3,6-DMFL; (e) pure 2,7-DMFL.

followed in higher excited states of DPC, and only more elaborate calculations can reveal this. It may well be that not all the species shown in Scheme 6 are discrete intermediates on excited state energy surfaces.

The laser-drop photolysis experiments demonstrate that high-intensity laser irradiation does cause carbene−carbene rearrangement to occur in solution, nominally at room temperature. There are three possible explanations: (i) a hot singlet state S_1 of the diphenylcarbene is formed, which then undergoes a very fast *thermal* carbene−carbene rearrangement; (ii) a higher excited singlet state S_n of DPC (most likely S_2) rearranges in a manner similar to S_1 to give fluorene; (iii) because of the possibility of surface crossings, the reaction could also be initiated from the excited triplet state, T_1. Conversion between upper excited states is expected to take place on a time scale of tens of picoseconds. Vibrational relaxation of the S_1 state of DPC takes place on a time scale of ~10 ps in cyclohexane.[12] Generally, vibrational relaxation of hot polyatomic molecules takes place in tens to hundreds of picoseconds in solution,[23] and molecular rearrangements may take place on a similar time scale.[24] Although chemical activation is usually restricted to the gas phase,[25] it is sometimes invoked to explain unexpected reactivity in solution.[26]

Scheme 6. Diphenylcarbene-Fluorene Rearangement in the S_1 State[a]



[a] Relative energies + ZPVE in kcal/mol at the B3LYP/6-311+G**//B3LYP/6-31G* level.

The formation of 3,6-dimethylfluorene from DMPD was observed in all the laser-drop experiments. This is the *ortho,ortho′* bond forming reaction. The proportion of this route to fluorene appears to increase with increasing laser energy (Table 1), but it is always less than the carbene−carbene rearrangement route. The spin state responsible for *ortho,ortho′* coupling cannot be T_0 or S_1 because this route is not followed at all under FVT conditions.

■ CONCLUSION AND OUTLOOK

Laser-drop photolyses of *p,p′*-dimethyldiphenyldiazomethane, **8**, revealed that both 3,6-dimethylfluorene, **9**, and 2,7-dimethylfluorene, **10**, are formed. Formation of 3,6-DMFL corresponds to the *ortho,ortho′* bond forming reaction, but formation of 2,7-DMFL corresponds to the carbene−carbene rearrangement. The latter is the dominant reaction under all laser photolysis conditions investigated, but higher laser energy allows proportionately more *ortho,ortho′* coupling to occur. This is a normal outcome for competing reactions. The ratio of the two processes depends on the wavelength and the light intensity. A priori, three possible scenarios for the carbene−carbene rearrangement can be envisaged: (i) a hot singlet state S_1 of the diphenylcarbene undergoes a rapid *thermal* carbene−carbene rearrangement, although vibrational relaxation is expected to take place on a time scale of tens of picoseconds. (ii) A higher excited singlet state S_n rearranges in a manner similar to S_1 to give fluorene. (iii) An excited triplet state initiates the reaction, which may proceed via a surface crossing. Chemical activation[25] (hot molecules) in solution does not seem very likely in the present case, which involves a double carbene−carbene rearrangement. The advantage of the laser-drop method with high-intensity excimer lasers is that it allows two-photon photochemistry. Thus, it is likely that the rearrangement occurs in a higher excited state (S_2 or T_1). The *ortho,ortho′* coupling *must* be a reaction in a higher excited state, because it does not take place under normal FVT conditions, where only S_1 and T_0 are likely to be populated. Calculations of the reactivities of excited states (particularly S_2 and T_1) of these and other carbenes are now being planned.

■ EXPERIMENTAL SECTION

Diphenyldiazomethane (DPDM),[27] **1**, tetraphenylethylene (TPE),[1,4] **4**, 9,10-diphenylphenanthrene (DPP),[1,4] **5**, 9,10-diphenylanthracene (DPA), **6**,[1] *p,p′*-dimethyldiphenyldiazomethane (DMPDM), **8**,[23] 3,6-DMFL, **9**, and 2,7-DMFL, **10**,[17a,28] were prepared according to literature procedures, and fluorene (FL), **3**, was a commercial sample. Once prepared, diazo compounds were stored in the freezer. Due to slow decomposition over time, they were purified by column chromatography prior to photolysis using basic Al_2O_3 and hexane as eluent.

Steady-state fluorescence spectra were measured with a luminescence spectrometer using spectral grade hexanes. A spectral bandwidth of 5 nm in excitation and emission was used. Excitation wavelengths of 250 nm were applied, and the spectra were recorded in the range 280−480 nm. Cross-contamination of solutions was avoided at all times by washing the quartz cuvette with hexane, then measuring emission of hexane before proceeding to the next solution.

GC-MS analyses were performed on a quadrupole mass spectrometer connected to a gas chromatograph equipped with a BP-5 capillary column (30 m × 0.25 mm with 0.25 μm phase thickness; He carrier at 20 psi head pressure; injector 200 °C; detector 280 °C; column temperature 100−250 °C, programmed at 16 °C/min).

Purification of laser photolysis mixtures was first done by thin-layer chromatography (SiO_2 60, F-254, 1, or 0.25 mm thickness). The plates were normally eluted 2 to 3 times using spectral grade hexanes. All fractions recovered from the plates were extracted once with spectral grade hexane. The hexane extracts were then analyzed by fluorescence spectroscopy for fluorene/dimethylfluorene emission. All fractions containing fluorene/dimethylfluorene were then extracted several times with distilled chloroform or hexane until no more fluorene/dimethylfluorene emission was detected. The extracts were then combined and concentrated. The residue obtained was purified once or twice more by preparative TLC prior to GC analysis.

Purifications by HPLC used a Si-80-125-C5 normal phase analytical column (eluent, hexane; flow rate, 1 mL/min; fluorescence detection λ_{exc} 250 nm, λ_{em} 320 nm).

Characterization of the dimethylfluorene isomers in the various laser photolysis mixtures was done by gas chromatographic analysis on either a BP21 or a BP10 capillary column (50 m × 0.22 mm with 0.25 μm phase thickness; He carrier at 42 psi head pressure; injector 200 °C; detector 280 °C; column temperature 100−180 °C, programmed at 16 °C/min. Separation of 3,6-dimethylfluorene (3,6-DMFL), **9**, and 2,7-dimethylfluorene (2,7-DMFL), **10**, was achieved on both of these columns. After two to three purifications by preparative TLC, photolysis mixtures were first analyzed on the BP21 column to determine the ratio of both isomers present. A control injection of a 1:1 standard solution of 3,6-DMFL and 2,7-DMFL in hexane confirmed that both isomers had the same detector response on the BP21 column. The dimethylfluorene isomers were identified by co-injection with authentic materials on the two different capillary columns described above. To avoid contamination, three different syringes were used, and blank (solvent only) injections were done after each GC analysis.

Photolyses. All photolyses were conducted by using spectral grade hexane, which was distilled over anhydrous $MgSO_4$ using a distillation column (45 cm × 2 mm i.d.) filled with glass O-rings. Solutions of diazo compounds were purged (in the dark) with ultrahigh purity N_2 for at least 20 min prior to irradiation. For the static lamp irradiations, the purging of solutions was done in the quartz vessels used for photolysis. For laser-drop irradiations, the purging of solutions was done in round-bottom flasks capped with rubber septa, which had been bleached in toluene.

Low-Intensity Irradiations. Solutions of DPDM, **1**, in hexane at either 5×10^{-5} M (1.5 mg/150 mL) or 1×10^{-3} M (29.6 mg/150 mL) were photolyzed using a 40 W low-pressure Hg lamp (254 nm). Solutions were magnetically stirred during photolysis. The progress of the reaction was monitored by emission spectroscopy or UV−visible spectroscopy. Photolyzates were then concentrated on a rotary evaporator. The residue obtained was chromatographed on silica using a Pasteur pipet and eluted with hexane. All chromatography fractions collected (1−2 mL) were analyzed by emission spectroscopy.

Laser-Drop Photolyses. The general procedure described in the literature[18] was followed with some modifications. The beam from either a Lambda Physik EMG 101 MSC excimer laser (Xe/HCl/Ne, 308 nm, ∼15 ns) or a Lumonics Excimer-600 laser (Kr/F_2/Ne, 248 nm, ∼15 ns) was focused by means of a quartz lens ($F = 200$) into a drop of the photolysis solution suspended from a 2-in. syringe needle (20 gauge). The flow rate of the solution was controlled by a syringe pump. The lasers were run at a constant repetition rate of 10 Hz in order to obtain high laser power. The N_2-purged solution (ca. 45 mL) was syringed out of the purging vessel using a 50 mL gastight syringe with Teflon-tipped plunger just prior to photolysis. A volume of 250 mL of solution to be photolyzed was prepared at a time and stored in the dark prior to N_2-purging.

*Laser-Drop Photolysis of Diphenyldiazomethane, **1**.* A solution of 7.8 mg of DPDM in 750 mL of hexane (5×10^{-5} M) was photolyzed at 308 nm (75−85 mJ/pulse over 4 days). The photolyzate was concentrated on a rotary evaporator and purified by preparative TLC (see details above). GC-MS analysis permitted the identification of fluorene by direct comparison with authentic material.

*Laser-Drop Photolyses of p,p′-Dimethyldiphenyldiazomethane, **8**.* A solution of 17.4 mg of *p,p′*-dimethyldiphenyldiazomethane (DMPDM) in 1.5 L of hexane (5×10^{-5} M) was photolyzed at 308 nm (85−90 mJ/pulse over 5 days). After purification of the photolyzate, GC analysis using the BP21 capillary column revealed the presence of both 3,6-DMFL and 2,7-DMFL in a ratio of 1.0:15. DMPDM, 12.4 mg in 1.0 L of hexane, was photolyzed by LDP at 248 nm (75−180 mJ/pulse over 3 days). A mixture of 3,6-DMFL and 2,7-DMFL in a ratio of 1.0:6.6 was obtained. DMPDM, 11.6 mg in 1.0 L of hexane, was photolyzed by LDP at 248 nm (85−95 mJ/pulse) over 2 days. A mixture of 3,6-DMFL and 2,7-DMFL in a ratio of 1.0:8.4 was obtained. The presence of both isomers was confirmed by co-injection on the BP21 column.

*Laser-Drop Photolysis of 2,7-Dimethylfluorene, **10**.* A solution of 1.0 mg of 2,7-DMFL **10** in 250 mL of hexane (2×10^{-5} M) was photolyzed by LDP at 248 nm (115−120 mJ/pulse). The photolyzate was analyzed by emission spectroscopy and by capillary GC (BP21 column). No 3,6-DMFL was detected. Only 2,7-DMFL was present.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S5 showing additional emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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