of Campaigne and Le Suer.[26] 3-Thenoic acid (24 g) was then refluxed in thionyl chloride (100 ml) with two drops of pyridine until a homogeneous solution was obtained. The excess thionyl chloride was then removed by distillation leaving 28 g (100%) of crude 3-thienoyl chloride which was not further purified.

The crude 3-thienoyl chloride (8 g) was dissolved in anisole (150 ml) and aluminum chloride (13 g) was added in portions, with stirring. A slightly exothermic reaction occurred giving a deep red solution which was stirred for 15 min and then poured into water (500 ml). The organic layer was separated and the aqueous layer extracted with ether (2 × 150 ml). The ether extracts were washed twice with 10% aqueous potassium hydroxide and (250 ml) twice with water (500 ml) and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a brown solid. Recrystallization of this solid from methanol yielded 7.3 g (72%) of 3-(4-methoxybenzoyl)thiophene as colorless crystals: mp 67–67.5°; ir $\nu_{max}^{CHCl_3}$ 1640, 1600, 1574, and 1507 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62. Found: C, 66.12; H, 4.71.

Acknowledgment. This work was supported by a grant from the National Research Council of Canada.

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[26] E. Campaigne and W. M. Le Suer, "Organic Synthesis," Collect. Vol. IV, Wiley, New York, N. Y., 1963 p 919.

Photochemical Rearrangement Effected by Triplet Excitation Transmitted through a High Energy Moiety. Mechanistic and Exploratory Organic Photochemistry. LXXX[1,2]

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Abstract: 5,12-Dihydro-2,3-naphthacenobarrelene was synthesized. This is a molecule with a naphtho low triplet energy reservoir at one terminus which is attached by methylene groups to the benzo ring of the higher energy benzobarrelene moiety. Direct irradiation proved capable of selectively exciting the naphtho ring. Similarly, benzophenone sensitization delivered triplet excitation to the naphtho group. Fluorescence studies revealed only naphthalene-like emission. Parallel phosphorescence spectra also proved characteristic of a naphthalene chromophore. Yet both direct and sensitized photolyses afforded the corresponding semibullvalene. The quantum yields were $\phi = 0.36$. The similar reactivity in direct and sensitized runs suggests that rearrangement utilizes a triplet excited state. Thus, the 63 kcal/mol naphtho triplet excitation energy initially heavily localized at one end of the molecule proves available to the other end of the molecule as needed for vinyl–vinyl bonding in the di-π-methane rearrangement.

In previous studies we have shown that, like barrelene itself,[3] benzobarrelene,[4] 2,3-naphthobarrelene,[5] and 2,3-anthrabarrelene[2] all rearrange to give the corresponding substituted semibullvalene. Additionally, the rearrangements have been shown[2–5] to proceed by initial bridging of the two vinyl groups in the triplet excited states.

An intriguing question posed itself. This was whether in a molecule such as 5,12-dihydro-2,3-naphthacenobarrelene (**1**) triplet excitation delivered to the naphtho moiety could successfully effect the di-π-methane rearrangement.[3–5] Two impediments would seem to make such a result difficult. First, the vinyl–vinyl bridging occurs at a site quite remote from the excited naphtho group. Second, the triplet excitation would have to pass up an energy ladder through the benzo moiety; naphtho triplet excitation is slightly above 60 kcal/mol while the benzo moiety requires on the order of 80 kcal/mol for excitation.

Synthesis of Barrelene 1. An approach was selected which would generate dihydronaphthacyne (**9**). This could react with benzene to give barrelene **1**. We started with the readily available naphthalene-2,3-dicarboxylic anhydride.[6] This was condensed with tetralin by treating with aluminum chloride to give *o*-(1,2,3,4-tetrahydro-6-naphthoyl)naphthoic acid (**2**) which was cyclized to 1,2,3,4-tetrahydro-6,13-dioxopentacene (**3**) in hot sulfuric acid. Nitric acid oxidation of dione **3** to 5,12-dioxo-2,3-naphthacenedicarboxylic acid (**4**) was followed by cyclization with acetic anhydride to 5,12-dioxo-2,3-naphthacenedicarboxylic anhydride (**5**). Reaction of anhydride **5** with urea afforded 5,12-dioxo-2,3-naphthacenedicarboxyimide (**6**) which was converted to sodium 2-amino-5,12-dioxo-3-naphthacenecarboxylate (**7**) under Hofmann rearrangement conditions. Reduction of **7** with zinc under alkaline conditions furnished 2-amino-5,12-dihydro-3-naphthacenoic acid (**8**) which was then used as the dihydronaphthacyne precursor. An *in situ* method[7] employing isoamyl nitrite in benzene at 80° led to barrelene **1**, mp 285–287°, in yields ranging from 6 to 10% (note Chart I and the Experimental Section for the detailed synthetic procedure).

The structure assigned to barrelene **1** derives from

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[1] For paper LXXVIII see H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, **95**, 3970 (1973).

[2] For paper LXXIX of the series, note H. E. Zimmerman and D. R. Amick, *J. Amer. Chem. Soc.*, **95**, 3977 (1973).

[3] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

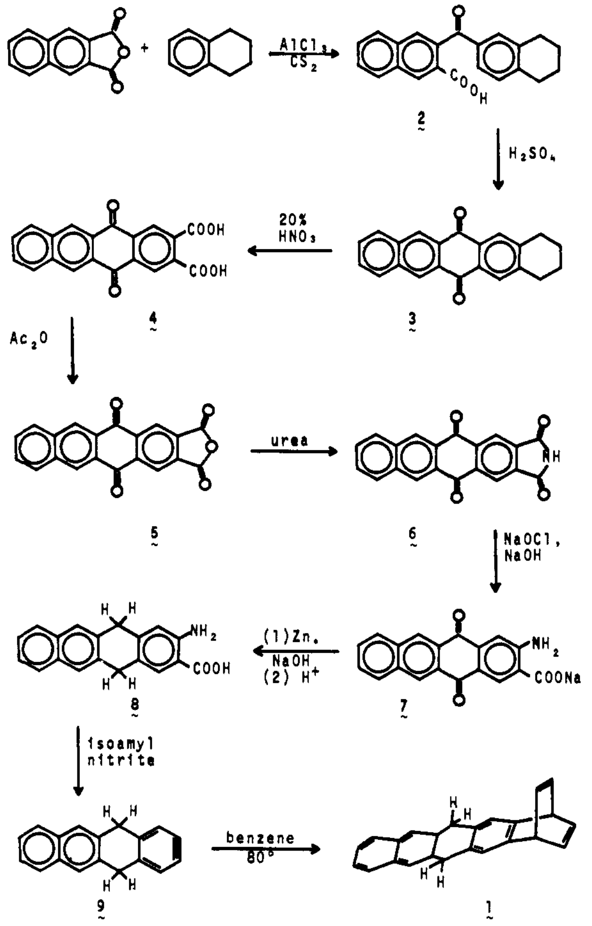
[4] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191, 6096 (1968).

[5] H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).

[6] (a) M. Freund and K. Fleischer, *Justus Liebigs Ann. Chem.*, **399**, 215 (1913); (b) K. Yogi, *J. Agr. Chem. Soc. Jap.*, **23**, 43 (1944); *Chem. Abstr.*, **45**, 5142 (1951).

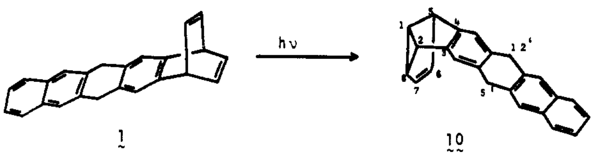
[7] L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).

Chart I. Synthesis of 5,12-Dihydro-2,3-naphthacenobarrelene



the synthetic method, the close agreement of the vinyl and bridgehead proton nmr pattern with that of the other aromatic barrelenes,[2,4,5] and lastly the distinctive uv absorption indicating an intact naphtho moiety (note the Experimental Section).

Photochemistry of Dihydronaphthacenobarrelene 1. Direct irradiation of barrelene **1** proceeded in an uncomplicated fashion to afford 5,12-dihydro-2,3-naphthacenosemibullvalene (**10**). The nmr spectrum proved conclusive in establishing the semibullvalene structure. Thus, the methylene groups at carbons 5′ and 12′ appeared as an unresolved, sharp singlet which integrated for four hydrogens. As in the previously studied semibullvalenes H-1 appeared as a quartet, being equally split by the three adjacent hydrogens. H-2 appeared as a triplet; this is again semibullvalene-like. Characteristically, H-5 appeared as a double doublet and H-8 was a triplet of doublets. The coupling constants and chemical shifts were those expected from the semibullvalene structure and are compared with the data for 2,3-naphthosemibullvalene in Table I (note also the Experimental Section). Thus, the rearrangement can be depicted as



The reaction proved to be preparatively useful in that it could be carried to high conversions with only slow loss of product. This facile conversion was reflected in a relatively high quantum yield of $\phi = 0.36$. The efficiencies were obtained using the semimicro optical bench described by us earlier.[8] Assays were made using high speed liquid chromatography as reported in an acylic di-π-methane study;[9] a triphenylethylene internal standard was employed.

Table I. Nmr Data for Semibullvalene **10** and 2,3-Naphthosemibullvalene

Description and assignment	Signal position, τ Naphtho-SB	Signal position, τ SB-10	Coupling constant, cps Naphtho-SB	Coupling constant, cps SB-10
Multiplet, aromatic	2.36–2.93	2.12–3.28		
ABX quartet, vinyl next to benzyl, H-6	4.49–4.63	4.32–4.48	$J_{67} = 5.0$ $J_{56} = 2.0$	$J_{67} = 5.0$ $J_{56} = 2.0$
ABX quartet, vinyl next to cyclopropyl, H-7	4.83–4.96	4.77–4.87	$J_{67} = 5.0$ $J_{78} = 2.0$	$J_{67} = 5.0$ $J_{78} = 2.0$
ABX quartet, benzylic and allylic, H-5	6.00–6.13	5.94–6.06	$J_{56} = 2.0$ $J_{15} = 6.5$	$J_{56} = 2.0$ $J_{15} = 7.0$
ABCD quartet, interior cyclopropyl, H-1	6.63–6.94	6.58–6.86	J_{15}, J_{18}, and $J_{12} = 6.5$	J_{15}, J_{18}, and $J_{12} = 7.0$
ABC triplet, cyclopropyl and benzylic, H-2	6.98–7.22	6.90–7.06	J_{12} and $J_{28} = 6.5$	J_{12} and $J_{28} = 7.0$
ABCX triplet of doublets, cyclopropyl H-8	7.39–7.62	7.22–7.42	$J_{78} = 2.0$ J_{18} and $J_{28} = 6.5$	$J_{78} = 2.0$ J_{18} and $J_{28} = 7.0$

Sensitization studies used benzophenone. It was observed that the quantum yield for disappearance of barrelene **1** was again $\phi = 0.36$. Quantum yields for appearance of semibullvalene product **10** were lower ($\phi = 0.07$), however, due to side reactions. Thus, the sensitized quantum yields have to be taken as lower limits. In another test an equimolar amount of naphthalene and benzobarrelene was photolyzed at the usual concentration and with the usual 292–334-nm light. In contrast to the intramolecular situation, no reaction of the benzobarrelene was observable. This, however, is not totally surprising and may arise from a variety of factors. One is that an exciplex formed in this manner is expected to have a rate of dissociation leading to a very low effective contact time of the pair.

One further point of interest was a determination of the nature of emission from the excited states of barrelene **1**. It was found that the fluorescence of barrelene **1** had a maximum at 341 nm and proved to be quite similar in wavelength and general shape to the fluorescence of naphthalene itself. The fluorescence quantum yield was measured as $\phi_f = 0.59$. The emission was at considerably longer wavelength than the fluorescence of benzobarrelene at 289 nm. Thus it appears to be the naphtho moiety which emits from the singlet.

Turning to emission from the triplet, we found phosphorescence of barrelene **1** at 77°K in isopentane–methylcyclohexane (1:4) glass to be very similar to that of naphthalene itself. Thus the O–O band was

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[8] H. E. Zimmerman, *Mol. Photochem.*, 3, 281 (1971).

[9] H. E. Zimmerman, R. J. Boettcher and W. Braig, *J. Amer. Chem. Soc.*, 95, 2155 (1973).

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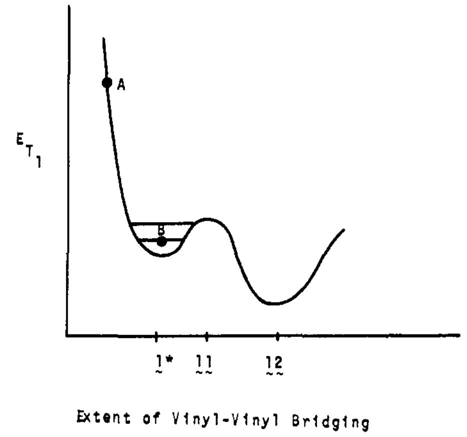


Figure 1. Mechanism of energy coupling between the naphtho triplet and the vinyl–vinyl moiety.

at 456 nm (*i.e.*, E_T = 62.7 kcal/mol) compared with 469 nm for naphthalene; additionally the vibrational structure was quite similar for the two compounds. In contrast, the phosphorescence of benzobarrelene was at shorter wavelength with a O–O band at 361 nm (*i.e.*, 79.3 kcal/mol). Hence emission from the triplet of barrelene **1** can be seen to be a manifestation of the naphtho moiety as was the case for fluorescence.

Interpretative Discussion. The first point requiring discussion is an intriguing one. This concerns the point that both in the singlet and in the triplet excited state the evidence indicates that the excitation energy is heavily localized in the naphtho end of the molecule. This is not surprising since this moiety has a lower energy of excitation than the benzobarrelene chromophore, and one would expect only small coupling with the benzobarrelene moiety. What one means by energy localization is just that the excited-state wave function differs from the ground-state wave function primarily in one part of the molecule, here the naphtho moiety.

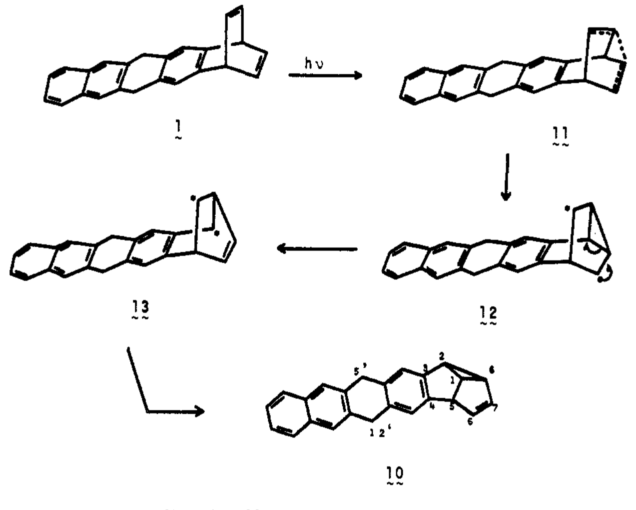
Despite this energy localization and the fact that this rearrangement is known to proceed *via* vinyl–vinyl bridging[2,4,5] at the other end of the molecule, the rearrangement to the corresponding semibullvalene **10** proceeds smoothly and relatively efficiently (*i.e.*, ϕ = 0.36). In fact, the sum of the reaction and fluorescence quantum yield (ϕ_f = 0.59) is close to unity, evidencing lack of inefficiency.

In order to understand this bizarre behavior, it is necessary to discuss the nature of the excited state reacting. It does appear from previous studies that in the aromatic barrelenes it is the triplet excited states which rearrange to give semibullvalenes.[2-5] For example, in the case of 2,3-napthobarrelene facile intersystem crossing followed direct irradiation and the ensuing triplet rearranged.[5] The same rearrangement could be effected with benzophenone sensitization. In the present situation, sensitization did afford the semibullvalene product, but not as cleanly as in the direct runs. The difference appears to be due to reactions involving benzophenone itself and does not change the conclusion that the triplet, when generated, does rearrange to semibullvalene **10**. Analogy suggests that the semibullvalene obtained in direct irradiation runs derives from facile intersystem crossing, as in the naphthobarrelene situation, followed by rearrangement of the triplet.

Since the triplet excitation energy of the benzobarrelene moiety can be estimated from the triplet energy of benzobarrelene itself as 79.3 kcal/mol, it is clear that the rearrangement does not involve *simple* energy transfer intramolecularly from the naphtho moiety to the benzobarrelene portion of the molecule. However, it is possible that the naphtho moiety's energy is sufficient to transfer to a partially vinyl–vinyl bridged structure. This corresponds to a type of nonvertical energy excitation,[10] namely a special case where the nonvertical geometry is along the reaction coordinate (*i.e.*, **11**). A partially bridged vinyl–vinyl grouping should have a triplet excitation energy of *ca.* 57 kcal/mol.[4,5] Thus, as the two vinyl moieties approach one another, the strain energy incurred is offset to some extent by lowering of the electronic energy of this portion, and leakage of electronic excitation energy from the naphtho to the vinyl–vinyl portion of the molecule occurs. That a barrier still exists, however, in the vinyl–vinyl bridging process is evident from the observation of phosphorescence from the initial naphthalene-like triplet rather than from some lower energy species (*i.e.*, geometrically deformed or having extended conjugation). The energy leakage process is illustrated in Figure 1. Two extreme possibilities exist. One is that the energy to surmount the barrier is provided by *kT* (*i.e.*, normal activation by thermal energy of the enviroment). The other is that intersystem crossing of the barrelene gives a sufficiently high energy vibrational state of T_1 that there is a modest probability that the barrier will be overcome within a molecular vibration. These two possibilities correspond to the triplet being generated at points A and B in Figure 1.

Finally, the gross reaction mechanism is outlined in Chart II.

Chart II. Mechanism for Rearrangement of Barrelene **1**



Experimental Section[11]

Photolysis Equipment. Large scale quantitative runs were made with the Black Box apparatus[8] previously described[12] using a

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[10] J. Saltiel and G. S. Hammond, *J. Amer. Chem. Soc.*, **85**, 2516 (1963).

[11] All melting points were taken on a hot stage apparatus calibrated with known compounds.

[12] H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schroder, *J. Amer. Chem. Soc.*, 93, 3662 (1971).

1000-W AH6 high-pressure mercury arc in a parabolic reflector 14.0 cm in diameter and 750-ml quartz-faced cells. Small scale runs were made on the organic chemists' optical bench described earlier;[8,12] this utilized a Bausch and Lomb high-intensity monochrometer with a HBO 200-W high-pressure lamp and 40-ml, 10-cm cells. In both cases a beam splitter[12] and ferrioxalate actinometry[13] were used.

A filter combination was used in the Black Box apparatus having three 2.4-cm path length filter cells: cell I, 1 mol of nickel sulfate hexahydrate/l. of 10% sulfuric acid; cell II, 2 mol of cobalt sulfate heptahydrate/l. of 10% sulfuric acid; cell III, 10^{-4} mol of bismuth trichloride/l. of 20% hydrochloric acid (by volume); transmission 255–305 nm, max at 283 nm (46%).

For both direct and sensitized runs, vanadous-purified nitrogen[14] was bubbled through the solution for 45 min prior to photolysis, and was continued during the irradiation.

Solvent. Cyclohexane was stirred with one-tenth of its volume of 10% fuming sulfuric acid for 8 hr, washed with 10% aqueous potassium hydroxide, dried over magnesium sulfate, and distilled from calcium hydride.

***o*-(1,2,3,4-Tetrahydro-6-naphthoyl)naphthoic Acid.** A mixture of 50.0 g (0.252 mol) of naphthalene-2,3-dicarboxylic anhydride, 40.0 g (0.300 mol) of tetralin, and 80.0 g of aluminum chloride in 1000 ml of carbon disulfide was refluxed for 2 hr. Removal of the solvent *in vacuo*, hydrolysis, and filtration was followed by crystallization from isopropyl alcohol to give 65 g (78%) of the desired acid: mp 241°; ir (Nujol) 3.2–4.4, 5.95, 6.13, 6.23, 6.36, 6.66, 7.08, 7.51, 7.69, 7.87, 8.08, 8.16, 8.29, 8.52, 8.79, 9.00, 10.49, 11.20, 11.82, 12.60, 12.82, 13.03, 13.32 μ; nmr (DMSO-d_6) τ 1.54 (s, 1 H, acid), 1.82–3.14 (m, 9 H, arom), 7.52 (m, 4 H, CH_2), 8.54 (br s, 4 H, CH_2).

While repeated recrystallization from isopropyl alcohol gave impure material, recrystallization from benzene afforded a 1:1 benzene adduct that analyzed well.

Anal. Calcd for $C_{28}H_{24}O_3$: C, 82.39; H, 5.87. Found: C, 82.33; H, 5.92.

1,2,3,4-Tetrahydro-6,13-dioxopentacene. A mixture of 10.0 g (0.0303 mol) of *o*-(1,2,3,4-tetrahydro-6-naphthoyl)naphthoic acid and 80 ml of concentrated sulfuric acid was heated at 80° for 7 min and then poured onto ice. Four runs of this type were further worked up together. The crude product was filtered and washed thoroughly with water. The moist material was dissolved in chloroform, washed with saturated ammonium sulfate solution, and filtered. The chloroform solution was passed through 2.5 cm of silica gel and reduced to 250 ml. The yellow precipitate was filtered and washed with small amounts of chloroform and then benzene to afford 16.6 g (44%) of the desired dione, mp 312–316°. This product was used in the next step without further purification. Recrystallization from chlorobenzene followed by sublimation afforded pure 1,2,3,4-tetrahydro-6,13-dioxopentacene: mp 321–322°; ir (Nujol) 5.99, 6.17, 6.26, 6.31, 6.41, 7.04, 7.52, 7.79, 8.42, 10.14, 10.45, 10.63, 10.95, 13.23, 14.17 μ; nmr ($CDCl_3$) τ 1.20 (s, 2 H, arom), 1.8–2.5 (m, 6 H, arom), 7.07 (m, 4 H, CH_2), 8.13 (m, 4 H, CH_2).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.54; H, 5.12.

5,12-Dioxo-2,3-naphthacenedicarboxylic Acid. A mixture of 40.0 g (0.128 mol) of 1,2,3,4-tetrahydro-6,13-dioxopentacene and 800 ml of 20% nitric acid was stirred under reflux for 48 hr. The product was filtered, water washed, dried, and thoroughly extracted with hot chloroform to leave 38.0 g of crude 5,12-dioxo-2,3-naphthacenedicarboxylic acid which was used in the next step without further purification. The infrared spectrum of the crude diacid showed peaks at: (Nujol) 2.8–4.8, 5.86, 5.98, 6.19, 6.31, 6.57, 7.82, 9.08, 10.16, 10.33, 10.70, 12.60, 13.18, 13.86, 14.58 μ.

The mass spectrum (70 eV) showed the molecular ion at m/e 346.048 (calcd for $C_{20}H_{10}O_6$, 346.049).

5,12-Dioxo-2,3-naphthacenedicarboxylic Anhydride. A mixture of 40.0 g of 5,12-dioxo-2,3-naphthacenedicarboxylic acid and 800 ml of tetrahydrofuran was stirred at reflux for 12 hr. Filtration gave 20 g of undissolved starting material; the filtrate was concentrated to 400 ml, combined with 140 ml of acetic anhydride, and refluxed for 40 min. The cooled mixture was filtered and the product rinsed with tetrahydrofuran to afford 10.0 g (53%) of crude anhydride which was used without further purification.

A small sample was purified as follows: 4.00 g of the anhydride was dissolved in 40 ml of hot 2% sodium hydroxide. Addition of saturated sodium chloride solution gave a dark precipitate which was filtered. The sodium salt of the diacid was collected from the cooled filtrate, rinsed with methanol, and dissolved in hot water. Acidification gave the free diacid which was collected and reacted with acetic anhydride (*vide supra*) to give 5,12-dioxo-2,3-naphthacenedicarboxylic anhydride: mp >360°; ir (Nujol) 5.40, 5.60, 5.95, 6.21, 6.33, 7.70, 8.03, 8.32, 10.30, 10.93, 11.20, 13.05, 13.56, 14.08 μ.

Anal. Calcd for $C_{20}H_8O_5$: C, 73.17; H, 2.46. Found: C, 72.44; H, 2.46.

The mass spectrum (70 eV) showed the molecular ion at m/e 328.037 (calcd for $C_{20}H_8O_5$, 328.037).

5,12-Dioxo-2,3-naphthacenedicarboxyimide. A mixture of 2.00 g (6.1 mmol) of 5,12-dioxo-2,3-naphthacenedicarboxylic anhydride, 15.0 g of urea, and 240 ml of glacial acetic acid was stirred rapidly at reflux for 3 hr. The cooled mixture was filtered and the solid thoroughly washed with acetic acid and then benzene to afford 1.4 g (70%) of relatively pure imide. Recrystallization from nitrobenzene at 175° afforded pure 5,12-dioxo-2,3-naphthacenedicarboxyimide: mp >360°; ir (Nujol) 3.05, 3.23, 3.29, 5.65, 5.82, 5.88, 5.97, 6.20, 6.31, 7.14, 7.34, 7.47, 7.77, 8.27, 8.60, 8.67, 8.81, 9.00, 9.31, 10.26, 10.43, 10.67, 10.85, 13.13, 13.45, 13.96, 14.50, 15.71 μ.

Anal. Calcd for $C_{20}H_9NO_4$: C, 73.39; H, 2.77; N, 4.28. Found: C, 73.42; H, 2.77; N, 4.17.

Sodium 2-Amino-5,12-dioxo-3-naphthacenecarboxylate. To a mixture of 2.00 g (6.12 mmol) of 5,12-dioxo-2,3-naphthacenedicarboxyimide, 1.0 g of sodium hydroxide, and 40 ml of water was added 11.0 ml of a 0.58 *M* sodium hypochlorite solution[15] (6.38 mmol) at room temperature. The temperature was raised to 85° over 15 min. An orange precipitate was filtered after cooling. Further orange solid was salted out of the filtrate with sodium chloride. The combined sodium salts were rinsed with cold water to give 1.60 g (77%) of the desired sodium 2-amino-5,12-dioxo-3-naphthacenecarboxylate which was used without further purification.

A portion of the sodium salt was boiled in dilute hydrochloric acid and the resulting amino acid was recrystallized from tetrahydrofuran to give 2-amino-5,12-dioxo-3-naphthacenecarboxylic acid: mp >360°; ir (Nujol) 2.84, 2.87, 2.98, 3.1–4.5, 5.99, 6.20, 6.38, 7.16, 7.53, 7.86, 8.00, 8.31, 10.10, 10.95, 12.65, 13.35, 13.89, 14.35, 14.78 μ.

The mass spectrum (70 eV) showed the molecular ion at m/e 317.069 (calcd for $C_{19}H_{11}NO_4$, 317.068).

2-Amino-5,12-dihydro-3-naphthacenoic Acid. A suspension of 2.88 g of zinc dust in 27.0 ml of water was activated with 0.50 ml of Fehling's-I solution (36.64 g of copper sulfate pentahydrate dissolved in water and diluted to 500 ml).[16] To the mixture was added 2.0 g (5.9 mmol) of sodium 2-amino-5,12-dioxo-3-naphthacenecarboxylate, followed by 2.88 g of sodium hydroxide in 38 ml of water. The mixture was stirred rapidly at 100° for 3.5 hr. The zinc, coated with a red solid, was filtered from the cooled reaction mixture, dried, and added to 300 ml of tetrahydrofuran. Hydrochloric acid was added dropwise to the refluxing tetrahydrofuran mixture until pH 7 was reached and maintained for 1 min. The liquid was decanted from the zinc, acidified to pH 1, and cooled to 10°. The red precipitate was filtered (0.37 g) and the filtrate was saved. Upon rinsing with water the red solid turned to a deep blue color. The low resolution mass spectrum had a parent peak of 287 and the infrared spectrum showed both amine (2.88 and 2.97 μ) and carboxylic acid (3.1–4.5 μ) absorptions; this evidence indicated that the blue solid was not the desired amino acid, but instead the under-reduced 2-amino-3-naphthacenoic acid (25%). To the tetrahydrofuran filtrate was added 200 ml of water; the tetrahydrofuran was removed *in vacuo* and the resulting water mixture was filtered to afford 1.05 g (62%) of a tan solid which proved to be the desired 2-amino-5,12-dihydro-3-naphthacenoic acid. This product was used without further purification in the next step. The infrared spectrum exhibited peaks at: (Nujol) 2.86, 2.95, 3.1–4.5, 5.99, 6.15, 6.30, 6.47, 7.05, 7.65, 8.03, 8.33, 8.64, 10.55, 10.73, 11.88, 12.65, 13.58 μ.

The mass spectrum (70 eV) showed the molecular ion at m/e 289.110 (calcd for $C_{19}H_{15}N_1O_2$, 289.110).

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(13) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(14) L. Meites, *Anal. Chem.*, 20, 984 (1948).

(15) E. S. Wallis and J. F. Lane, *Org. React.*, 3, 281 (1940).

(16) L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, p 130.

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5,12-Dihydro-2,3-naphthacenobarrelene. A mixture of 100 mg (0.346 mmol) of 2-amino-5,12-dihydro-3-naphthacenoic acid and 700 ml of benzene (distilled from calcium hydride) was stirred under nitrogen during 1.5 hr at 78°. Isoamyl nitrite (0.20 ml, 1.5 mmol) was added all at once and the reaction continued an additional 5.5 hr at 78°. The green mixture was cooled and concentrated *in vacuo;* extraction with 3% chloroform in hexane was followed by thick layer chromatography (silica gel, GF_{254}; 20 cm × 20 cm plates). A single elution with 15% chloroform in hexane resulted in two separated mobile bands; the slower yellow band was ether extracted, concentrated, and submitted to thick layer chromatography (*vide supra*). A single elution with 15% ether–hexane again resulted in two separated mobile bands; the slower moving colorless band was ether extracted to afford 10.0 mg (9.45%) of the desired barrelene. Crystallization from ethanol followed by recrystallization from benzene gave pure 5,12-dihydro-2,3-maphthacenobarrelene: mp 285–287°; ir (KBr) 3.27, 3.33, 3.36, 3.42, 3.51, 3.58, 6.29, 6.38, 6.66, 6.72, 6.88, 7.05, 7.45, 7.55, 8.08, 8.15, 8.69, 9.05, 9.60, 10.52, 10.72, 11.10, 11.42, 11.69, 11.88, 12.58, 12.70, 13.41, 14.34, 14.90, 15.10 μ; nmr ($CDCl_3$) τ 2.10–3.00 (m, 8 H, arom), 3.13 (m, 4 H, vinyl), 5.12 (m, 2 H, bridgehead), 6.04 (s, 4 H, benzylic and naphthylic); uv max (cyclohexane) 230 nm (ε 88,200), 243 (16,900), 270 (6920), 279 (8080), 286 (7550), 318 (767), 325 (422).

Anal. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.95; H, 5.89.

5,12-Dihydro-2,3-naphthacenosemibullvalene from the Direct Photolysis of 5,12-Dihydro-2,3-naphthacenobarrelene. A solution of 50 mg (0.164 mmol) of 5,12-dihydro-2,3-naphthacenobarrelene in 750 ml of cyclohexane was irradiated with 4.2 mEinsteins through the 255–355-nm filter (*vide supra*) on the Black Box.[8] The photolysate was divided into five equal portions, each of which was concentrated, dissolved in 20 ml of hexane, and chromatographed on a 2.0 cm × 20 cm silica gel column (60–200 mesh). Elution with 0.5% ether–hexane and 25-ml fractions gave in fractions 7–9 6.4 mg of the desired semibullvalene. The photolysis thus afforded 32 mg (64%) overall. Crystallization from ethanol followed by recrystallization from benzene gave pure 5,12-dihydro-2,3-naphthacenosemibullvalene: mp 230–234° dec; ir (KBr) 3.25, 3.40, 3.48, 3.54, 5.79, 6.26, 6.32, 6.75, 6.85, 7.04, 7.43, 8.08, 9.11, 10.52, 10.72, 11.86, 12.04, 12.67, 12.79, 13.46, 13.75, 14.03, 15.03 μ; nmr ($CDCl_3$) τ 2.12–3.28 (m, 8 H, arom), 4.40 (ABX q, J_{67} = 5.0 cps, J_{56} = 2.0 cps, 1 H, vinyl H-6), 4.82 (ABX q, J_{67} = 5.0 cps, J_{78} = 2.0 cps, 1 H, vinyl, H-7), 6.00 (s, 4 H, benzylic and naphthylic H-9), 6.02 (ABX q, J_{56} = 2.0 cps, J_{15} = 7.0 cps, 1 H, benzylic and allylic H-5), 6.72 (ABCD q, J_{15} = J_{12} = J_{18} = 7.0 cps, 1 H, interior cyclopropyl H-1), 6.98 (ABC t, J_{12} = J_{28} = 7.0 cps, 1 H, cyclopropyl and benzylic H-2), 7.32 (ABCX t of d, J_{78} = 2.0 cps, J_{18} = J_{28} = 7.0 cps, 1 H, cyclopropyl and allylic H-8); uv max (cyclohexane) 229.5 nm (ε 88,400), 242 sh (26,000), 271 (6650), 280 (8300), 285 (8000), 314.5 (850), 318 (945), 330 (570).

Anal. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.08; H, 5.97.

Attempted Sensitization by Naphthalene of the Benzobarrelene to Benzosemibullvalene Rearrangement. A solution of 50 mg (0.325 mmol, 8.12×10^{-3} *M*) of benzobarrelene and 32 mg (0.25 mmol, 6.25×10^{-3} *M*) of naphthalene in 40 ml of cyclohexane was irradiated at 292–334 nm with 0.554 mEinstein on the optical bench. Analysis of the concentrated photolysate by nmr in $CDCl_3$ indicated the absence of benzosemibullvalene. A quantum yield of $\phi = 0.05$ would have given an easily observable amount of photoproduct.

Quantum Yield Determinations. The composition of the photolysates was determined *via* high-pressure liquid chromatography employing triphenylethylene as an internal standard. Analytical chromatograms were obtained on a Waters' ALC-100 liquid chromatograph equipped with a Waters' Model 77 uv detector having a 254-nm light source; two 2 ft × $^1/_8$ in. columns packed with Waters' Corasil-II were used in series and hexane was the eluent. A 18 ml/hr flow rate was employed. Integration of peak areas was achieved by tracing and weighing the peaks, and by planimetry. Absolute yields were obtained by determination of the peak area ratios utilizing authentic mixtures of known concentration of the internal standard (fastest moving component), 5,12-dihydro-2,3-naphthacenobarrelene (slowest moving component), and 5,12-dihydro-2,3-naphthacenosemibullvalene.

Quantum Yield of Direct Photolysis of 5,12-Dihydro-2,3-naphthacenobarrelene. A solution of 10 mg (0.0326 mmol) of 5,12-dihydro-2,3-naphthacenobarrelene in 40 ml of cyclohexane was irradiated at 292–334 nm with 0.0355 mEinstein on the optical bench. The photolysate was concentrated, combined with 2.07 mg of triphenylethylene, and dissolved in 25 ml of hexane. Column separation (*vide supra*) indicated 6.17 mg of unrearranged barrelene and 3.92 mg (0.0128 mmol) of the semibullvalene; $\phi_{form} = \phi_{dis} = 0.36$.

Quantum Yield of Sensitized Photolysis of 5,12-Dihydro-2,3-naphthacenobarrelene. A solution of 10 mg (0.0326 mmol) of 5,12-dihydro-2,3-naphthacenobarrelene and 59.5 mg (0.328 mmol) of benzophenone in 40 ml of cyclohexane was irradiated at 329–371 nm with 0.0373 mEinstein on the optical bench. The benzophenone absorbed >95% of the light. The photolysate was concentrated, combined with 1.41 mg of triphenylethylene, and dissolved in 25 ml of hexane. Column separation (*vide supra*) indicated 6.02 mg of unrearranged barrelene and 0.80 mg (0.0026 mmol) of the semibullvalene; $\phi_{dis} = 0.35$; $\phi_{form} = 0.07$. Additionally, a very slow moving peak suggested the formation of a benzophenone adduct.

Phosphorescence and Fluorescence Studies of 5,12-Dihydro-2,3-naphthacenobarrelene. All studies were carried out on an Aminco-Kiers spectrophosphorimeter using a rotating shutter for phosphorescence and a Xenon lamp in general. Phosphorescence studies of 5,12-dihydro-2,3-naphthacenobarrelene (5.0×10^{-4} *M*) in an isopentane–methylcyclohexane (1:4) glass at 77°K (after eight freeze–thaw–pump cycles) gave the O–O phosphorescence peak at 456 nm, corresponding to an energy of 62.7 kcal/mol. The fluorescence spectrum of **1** (5.0×10^{-4} *M*) was measured in cyclohexane at room temperature and showed a single broad band with a maximum at 341 nm.

It was possible to measure the approximate fluorescence quantum yield by using naphthalene as the standard ($\phi_f = 0.23$)[17] since the absorption and emission spectra of these two compounds were very similar in the 270–320- and 300–350-nm range, respectively. The concentration of a solution of naphthalene in cyclohexane was adjusted so that the absorbance matched that of a 5.0×10^{-4} *M* cyclohexane solution of 5,12-dihydro-2,3-naphthacenobarrelene over the 270–320-nm range. $\phi_{fl} = 0.59$.

Phosphorescence of Benzobarrelene. Phosphorescence studies (*vide supra*) of a 4.7×10^{-3} M benzobarrelene solution gave the O–O phosphorescence peak at 361 nm, corresponding to an energy of 79.3 kcal/mol.

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(17) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 104.