J. Am. Chem. Soc. **1992**, *114*, 7029–7034

the tube, whereupon the mixture turned deep-red. The tube was torch sealed under vacuum and an ESR spectrum of the mixture was taken at room temperature. This spectrum is shown in Figure 1.

Preparation of 1,2,2,3,3,4,4-Heptakis(2,6-diethylphenyl)-1-lithocyclotetrastannane (14). To a solution of 500 mg (0.36 mmol) of **3** in 5 mL of THF was added a solution of 42 mg (0.40 mmol) of LDA in 1 mL of THF at room temperature whereupon the solution turned orange-red. After the mixture was stirred at room temperature for 30 min, the solvent was removed in vacuo and the residue was taken up in a minimum volume of toluene. The resulting solution was then cooled to −40 °C, and after 18 h, 250 mg of the THF adduct of **14** (ca. 3:1 by ^{1}H NMR) was collected as an orange microcrystalline material (43% yield). ^{1}H NMR (toluene-d_8), see supplementary material. Anal. Calcd for $C_{70}H_{91}LiSn_4{\cdot}C_4H_8O$: C, 59.80; H, 6.71. Found: C, 59.56; H, 6.84.

Preparation of [4]$^-$[K,crypt]$^+$. In a glovebox, 10 mg (0.005 mmol) of **4**, 3 mg (0.005 mmol) of crypt, and 500 mg of 0.1% potassium amalgam were placed together in a quartz ESR tube equipped with a 14/20 ground glass joint. The tube was attached to a high-vacuum line and then ca. 2 mL of THF (dried over potassium mirror) was vacuum transferred to the tube. The tube was torch sealed under vacuum and an ESR spectrum obtained. This spectrum, which is consistent with that expected for [4]$^-$[K,crypt]$^+$, is shown in Figure 4 along with a best simulation which uses the following parameters: $g = 1.95$, $a(^{119/117}\mathrm{Sn}) = 22$ G (2 Sn atoms); $a(^{119/117}\mathrm{Sn}) = 50$ G (2 Sn atoms); $a(^{119/117}\mathrm{Sn}) = 65$ G (3 Sn atoms); line width = 6.5 G.

Acknowledgment. We thank Dr. Cynthia Day of Crystalytics Co. for the crystallographic analysis of **4** and the National Science Foundation (Grant CHE-9111861) for support of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available: ^{1}H NMR spectra of compounds **3**, **4**, and **14** and listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors for the crystallographic analysis of **4** (33 pages). Ordering information is given on any current masthead page.

Photochemical and Photophysical Studies of Bicyclo[4.3.0]non-1(6)-en-2-one

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Contribution from the Department of Chemistry, Faculty of Arts and Sciences, New York University, New York, New York 10003, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. Received June 17, 1991. Revised Manuscript Received May 18, 1992

Abstract: The properties of the lowest excited triplet state of bicyclo[4.3.0]non-1(6)-en-2-one (BNEN) have been investigated by nanosecond transient absorption spectroscopy, photoacoustic calorimetry, measurements of $^1O_2$ quantum yields, and photochemical studies in solution. Both the lifetime (1.4 μs) and the energy (74–76 kcal mol^{-1}) of the BNEN triplet reflect its exceptional conformational rigidity, which prohibits relaxation along the $^3(\pi,\pi^*)$ potential energy surface by twisting around the C=C bond. Fumaro- and maleonitrile quench the BNEN triplet at a diffusion-controlled rate by triplet energy transfer. This process leads to cis–trans isomerization of the alkenes. The BNEN triplet displays extensive self-quenching with $k_{sq} = 2.6 \times 10^7$ M^{-1} s^{-1}. This process involves intermolecular H-abstraction, but formation of dimeric triplet 1,4-biradicals cannot be excluded. The product of the former is a radical (**3**) with a lifetime of 4.1 μs. Its transient absorption spectrum (λ_{max} 299 nm) is hypsochromically shifted with respect to that of the BNEN triplet (λ_{max} 311 nm). The solvent effects on the photophysical properties suggest that the T_1 state of BNEN is a (π,π^*) state in acetonitrile and an (n,π^*) state in benzene. The BNEN triplet undergoes neither [2 + 2] cycloaddition reactions with itself, cyclopentene, fumaronitrile, or maleonitrile nor the lumiketone rearrangement, but readily abstracts H-atoms from itself, cyclopentene, and 2-propanol.

Introduction

The photoreactions and excited-state properties of cyclic enones continue to be of interest.[1] Recent studies indicate that the lifetimes, energies, and reactivity of enone triplets are determined by their ability to twist around the double bond.[2]

Conformationally flexible substituted cyclohexenones efficiently undergo [2 + 2] cycloaddition reactions as well as the lumiketone rearrangement. Recently, we reported[3] that in the photoreactions of 3-methylcyclohexenone with maleo- and fumaronitrile the formation of [2 + 2] cycloadducts occurs with complete loss of stereochemistry concomitant with isomerization of the starting alkene. This unequivocally demonstrates the intermediacy of a common set of rotationally equilibrated triplet 1,4-biradicals. The rate constants for quenching of 3-methylcyclohexenone by fumaro- and maleonitrile, combined with the quantum yields for formation of [2 + 2] cycloadducts and for cis–trans isomerization of the alkenes, suggest that energy transfer from the 3-methylcyclohexenone triplet to fumaro- and maleonitrile is not occurring, despite the favorable energetics of this process.[3] In contrast, the lumiketone rearrangement of structurally related 4,4-disubstituted cyclohexenones appears to involve a high degree of concertedness and is known to occur stereospecifically in a number of cases.[4]

[†] New York University.

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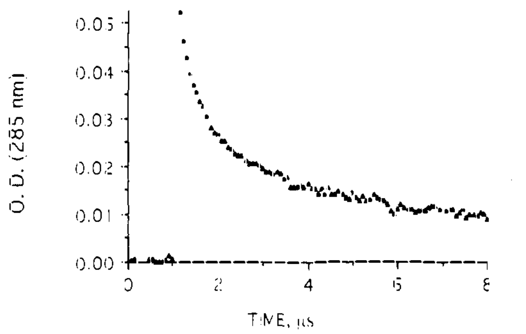


Figure 1. A 285-nm transient decay observed upon excitation of a degassed, 0.025 M solution of BNEN in acetonitrile at 337 nm, with a Molectron UV-24 nitrogen laser (pulse duration, ca. 8 ns; pulse energy, ca. 10 mJ/pulse).

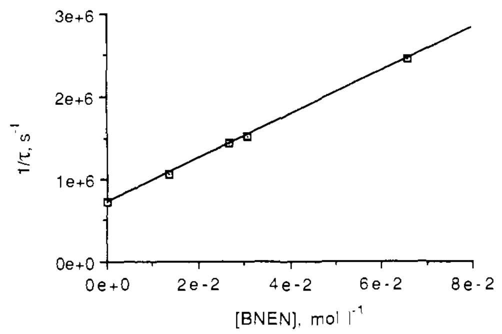
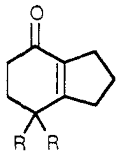


Figure 2. Self-quenching of the triplet in degassed acetonitrile solutions of BNEN: Stern–Volmer plot of the rate constant of triplet decay ($1/\tau$) vs the concentration of BNEN.

An increase in the conformational rigidity of cyclic enones increases both the energy and the lifetime of the triplet[2,5] and decreases the efficiency of the [2 + 2] cycloaddition reaction and the lumiketone rearrangement. Thus, 5,5-dimethylbicyclo-[4.3.0]non-1(6)-en-2-one (**1**) was observed to enter into a [2 + 2] photocycloaddition reaction only with diethyl acetylenedicarboxylate,[6] and not with simple alkenes. Furthermore, **1** does



1 R = Me
2 R = H

not undergo the lumiketone rearrangement, but rather undergoes atypical photoreactions, such as hydrogen abstraction from nontraditional H-donors such as *tert*-butyl alcohol and acetone.[7] Here we report the results of flash photolysis and reactivity studies of the parent system bicyclo[4.3.0]non-1(6)-en-2-one (BNEN, **2**). Because of its conformational rigidity, BNEN should be an excellent model compound for studying possible geometrical distortions of enone triplet states other than twisting around the C=C bond.

Results and Discussion

Upon laser flash photolysis of BNEN in acetonitrile at 337 nm,[2,8] a complex transient decay curve at 285 nm was observed (Figure 1). The decay data could be fit with a kinetic model involving two consecutive first-order decays. The lifetime of the short-lived species was increased from 400 to 900 ns upon decreasing the BNEN concentration from 0.0659 M to 0.0135 M, whereas the lifetime of the long-lived transient was 4.1 ± 0.7 μs,

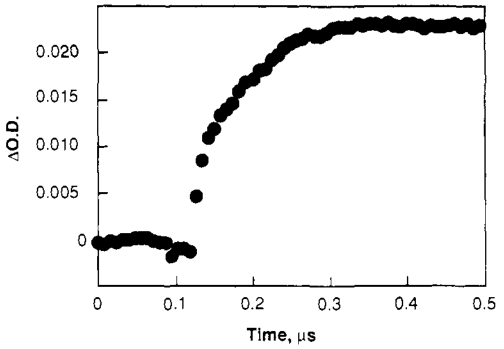


Figure 3. Growth of naphthalene triplet–triplet absorption at 420 nm after laser excitation of BNEN in benzene at 308 nm: naphthalene concentration, 1.5 mM; BNEN concentration, 0.04 M.

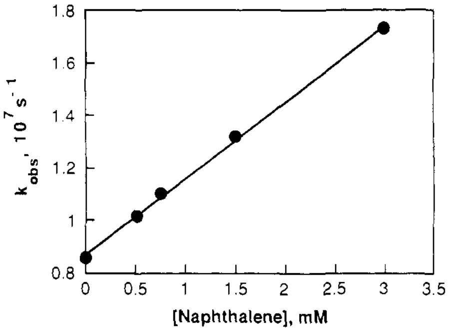


Figure 4. Pseudo-first-order rate constants for appearance of naphthalene triplet–triplet absorption as in Figure 3 as a function of naphthalene concentration.

independent of the concentration of BNEN. The possibility that the long-lived species decays by second- and not first-order kinetics cannot be excluded, given that experiments were not carried out using very long time bases, which might have permitted observation of transient decay back to baseline optical density. The contribution of the long-lived transient species to the transient optical density at 285 nm decreased from 21% to 15% with decreasing BNEN concentration. On the basis of these findings, the short-lived transient is assigned to the T_1 state of BNEN and the long-lived transient to a species emerging from self-quenching of this T_1 state. A plot of the decay rate (τ^{-1}) of the shorter-lived transient vs the concentration of BNEN is shown in Figure 2. It can be seen that this self-quenching process obeys Stern–Volmer kinetics, corresponding to a rate constant k_{sq} of $(2.6 \pm 0.3) \times 10^7$ M^{-1} s^{-1} and an extrapolated transient lifetime τ_{T^0} of 1.4 ± 0.2 μs at infinite dilution. Self-quenching kinetics were also observed in benzene, corresponding to a somewhat shorter limiting triplet lifetime (τ_T = 330 ns) and a slightly larger self-quenching rate constant, $k_{sq} = (1.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1}.

Confirmation that the short-lived transient is indeed the BNEN triplet comes from experiments in which BNEN (0.04 M) was irradiated at 308 nm in the presence of naphthalene (NA) in benzene solution, and the kinetics for appearance of NA triplet absorption at 420 nm were measured. A typical trace showing the growth of naphthalene triplet absorption is shown in Figure 3. The linear plot of the pseudo-first-order rate constants k_{obsd} for transient growth vs NA concentration in benzene is shown in Figure 4. The slope of this plot, 2.9×10^9 M^{-1} s^{-1}, is the rate constant for quenching of the BNEN triplet by NA and is close to the diffusion-controlled limit in benzene, while the intercept (0.86×10^7 s^{-1}) is the inverse of the lifetime of the BNEN triplet donor under these experimental conditions (116 ns). This value is indistinguishable experimentally from that of the BNEN triplet lifetime (128 ns) calculated from the triplet self-quenching parameters given above for 0.04 M BNEN in benzene. Thus, there can be no doubt that the more rapidly decaying transient is the BNEN triplet.

The limiting triplet lifetime of BNEN in acetonitrile of 1.4 μs is much longer than that of all other cyclohexenones studied to

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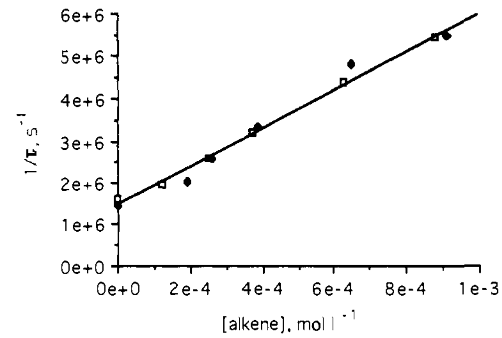

Figure 5. Stern–Volmer plot for the quenching of degassed 0.025 M acetonitrile solutions of BNEN by fumaronitrile (□) and maleonitrile (◆).

date[2] as well as of cyclopentenone,[9] consistent with the extreme conformational rigidity of BNEN, as argued previously.[2] The value of k_{sq} for the BNEN triplet is also higher than that observed for any other cyclohexenone triplet, but is still less than that of cyclopentenone, where $k_{sq} = 5.9 \times 10^8$ M^{-1} s^{-1} in acetonitrile.[9]

Quenching of the BNEN triplet by fumaro- and maleonitrile (FN and MN) in acetonitrile obeys first-order Stern–Volmer kinetics (see Figure 5) and occurs at essentially the diffusion-controlled rate ($k_q = (4.5 \pm 0.7) \times 10^9$ M^{-1} s^{-1}) with both alkenes. This suggests that quenching of the BNEN triplet by these alkenes occurs by energy transfer. This behavior contrasts with that of flexible cyclohexenones such as 3-methylcyclohexenone, for which the rate constants of triplet quenching by FN and MN are lower by an order of magnitude and for which a Schenck-like addition mechanism has been proposed.[3] In the BNEN–FN system, triplet energy transfer is thermodynamically favored, since the triplet energy of BNEN (74–76 kcal mol^{-1}), measured by photoacoustic calorimetry,[5] greatly exceeds that (59 ± 2 kcal mol^{-1})[10] of FN. Further support for energy-transfer quenching of the BNEN triplet by these alkenes comes from the observation that the photostationary ratio of MN to FN established upon irradiating a mixture of BNEN and FN in acetonitrile is 45:55, which is close to the 50:50 ratio observed upon irradiation of FN in the presence of a variety of triplet sensitizers (including benzophenone) that operate exclusively by an energy-transfer mechanism.[3,11] This ratio deviates considerably from the 70:30 ratio observed upon cis–trans photoisomerization of these alkenes in the presence of 3-methylcyclohexenone, which has been proposed to involve isomerization via rotationally equilibrated intermediate adduct 1,4-biradicals.[3] Analogous to the results of the self-quenching experiments, the absorption due to the long-lived transient derived from BNEN decreases with increasing concentrations of FN and MN. This is due to quenching by these alkenes of the formation of the secondary transient from BNEN triplets, since the lifetime of this long-lived species was independent of the alkene concentration.

The fact that the BNEN triplet lifetime in benzene, measured by nanosecond transient absorption spectroscopy, is considerably less than that in acetonitrile is consistent with the suggestion that the lowest triplet state (T_1) of BNEN has more n,π* character in benzene than in acetonitrile, where T_1 is closer to being a pure π,π* state. It is well-known that the lifetimes of ketone T_1 states generally increase as the π,π* character of the state increases.[12] In accord with this suggestion, the rate constant k_q^{O2} for quenching of the BNEN triplet by $^3O_2$, the quantum yield of formation of $^1O_2$, and the value of $k_q^{O2}\tau_T$ measured by monitoring the intensity of the $^1O_2$ phosphorescence intensity as a function of the oxygen concentration (see Table I) are all lower in benzene than in acetonitrile.[13] However, this downward trend should be viewed with caution, since these quantum yields were obtained at identical BNEN concentrations (2.29×10^{-2} M) and may reflect at least in part the difference in the values of k_{sq} for BNEN triplet in benzene and acetonitrile.

Table I. Solvent Dependence of Limiting Triplet Lifetimes (τ_T), Rate Constants for Triplet Self-Quenching (k_{sq}) and for Triplet Quenching by Oxygen ($k_q(O_2)$), Quantum Yields of Singlet Oxygen Formation ($\Phi(^1O_2)$), and $k_q(O)_2\tau_T$ Values for BNEN

solvent	k_{sq} (M^{-1} s^{-1})[a]	τ_T (μs)[a]	$k_q(O_2)$ (M^{-1} s^{-1})[a]	$k_q(O_2)\tau_T$[b]	τ_T (μs)[b]	$\Phi(^1O_2)$[b]
CH_3CN	2.6×10^7	1.4	4.6×10^9	15 500	3.7	0.58
C_6H_6	1.2×10^8	0.33	2.6×10^9	1300	0.5	0.36

[a] From nanosecond transient absorption spectroscopy. [b] From $^1O_2$ yields, derived from $^1O_2$ phosphorescence intensities.

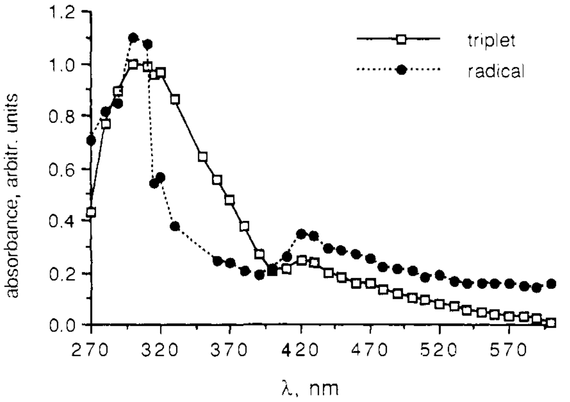

Figure 6. Transient absorption spectra of the triplet and of the radical species (3) produced by triplet self-quenching, generated by laser excitation (337 nm) of a degassed 0.025 M solution of BNEN in acetonitrile. Points represent the relative initial optical densities measured at each wavelength on flash excitation of the BNEN solution, at time delays of 120 ns and 3.5 μs for the BNEN triplet and radical 3, respectively.

The triplet energy of BNEN in acetonitrile solution measured by time-resolved photoacoustic calorimetry (PAC) using two different techniques in different laboratories (see Experimental Section for details) is 74 ± 2 (at high optical density) and 76 ± 7 (at low OD) kcal mol^{-1}. These values for the energy of the relaxed T_1 state of BNEN are the highest yet measured for any cyclohexenones[2,5] and are even higher than that recently found for cyclopentenone,[14] consistent with the extreme structural rigidity of BNEN.[5]

In acetonitrile, the spectrum of the long-lived transient (λ_{max} 299 nm, Figure 6) is shifted hypsochromically relative to that of the BNEN triplet (λ_{max} 311 nm, Figure 6) and is roughly similar in appearance to the transient spectrum of the $PhCOCMe_2$ radical formed by cleavage of $PhCOCMe_2SO_2Ph$[15a] and spectra of radicals of type PhC(OR)COPh (R = Et_3Si, Bu_3Sn, and Bu_3Ge) which have λ_{max} 360–380 nm.[15b] This prompts us to suggest that self-quenching of the BNEN triplet involves in part intermolecular H-abstraction, leading to radicals of type **3**, although such a species ought to show second- rather than first-order decay. As stated earlier, the data do not exclude decay of this species by second-order kinetics. No better spectral model for radicals analogous to **3** seems to be available in the literature, to the best of our knowledge. The formation of long-lived intermediates by self-quenching of the BNEN triplet is also indicated by PAC data, which showed that, upon laser excitation (337 nm) of BNEN at a concentration (0.12 M) where self-quenching is a dominant

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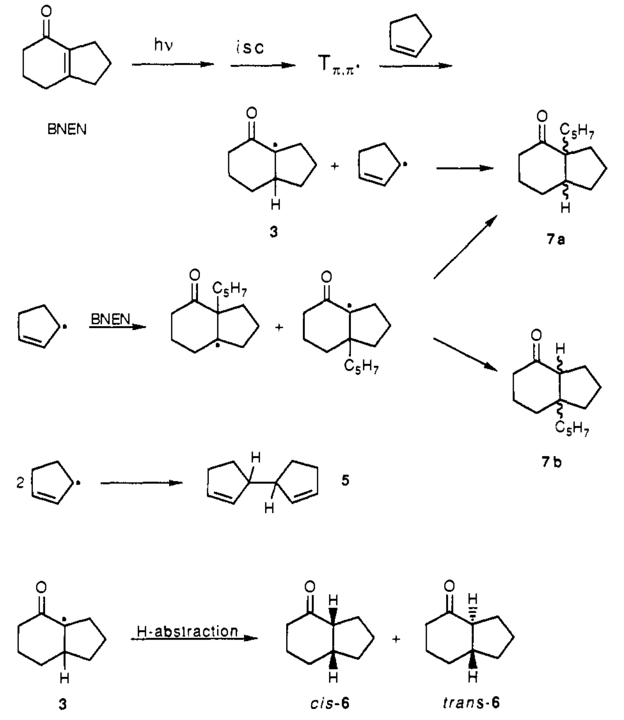
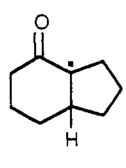
Scheme I



process, ca. 60% of the excitation energy is not returned as heat within the 2-μs experimental observation window. Quenching of the BNEN triplet by cyclohexane in benzene gave a linear Stern–Volmer plot with $k_q = (2.5 \pm 0.3) \times 10^6\ s^{-1}$, which is somewhat larger than values of k_q measured for H-abstraction reactions by typical (n,π*) and (π,π*) ketone triplets.[16]



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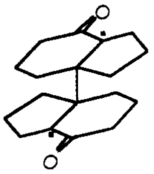
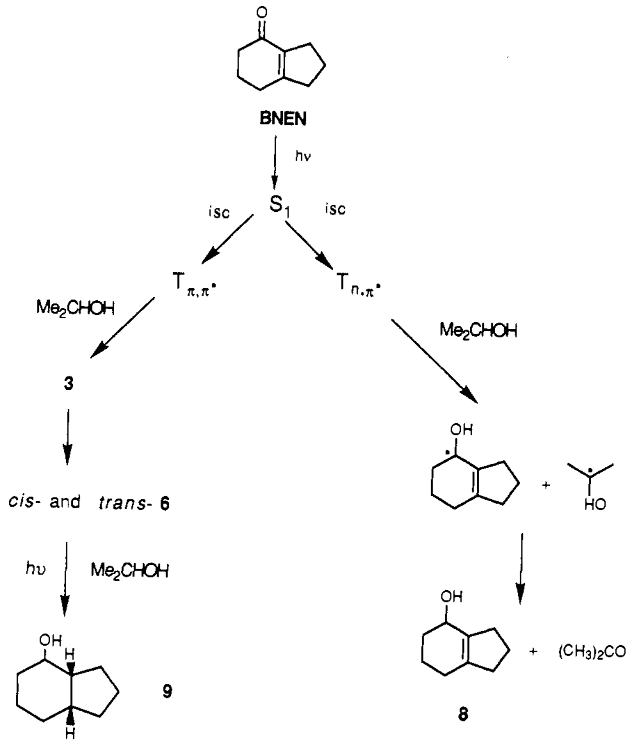


4

The possibility that triplet self-quenching of BNEN leads to an intermediate triplet 1,4-biradical (**4**) en route to [2 + 2] photodimers, by analogy with the behavior of cyclopentenone[2,9] or 3-methylcyclohexenone,[3] must be considered. In contrast to cyclopentenone,[17] irradiation of BNEN (0.05–0.3 M) in acetonitrile does not produce [2 + 2] cyclodimers, even in trace quantities, according to GC/MS data. However, since ring closure of dimeric biradicals of type **4** (head-to-head as well as head-to-tail) would lead to strained propellanes, it might not occur in competition with fragmentation to give two ground-state BNENs. Therefore, formation of the long-lived transient by intermolecular H-abstraction might represent only a minor self-quenching pathway. The lifetime of this transient species (4.1 ± 0.7 μs, see above) is incompatible with an intermediate triplet 1,4-biradical, for which a much shorter lifetime (ca. 20–100 ns) is expected.[2,9,18]

Irradiation of BNEN under different conditions consistently resulted in products derived from H-abstraction by the triplet. Upon irradiation of BNEN (0.05 M) in cyclopentene (CP), the primary photoproducts observed using GC/MS are 1,1′-bi-2-cyclopentenyl (**5**), minor quantities of *cis*- and *trans*-**6** (4:1 ratio), five 1:1 BNEN–CP adducts (**7**, *m/e* 204), and four 2:1 BNEN–CP adducts (*m/e* 272). The latter are presumably secondary photoproducts. These various products derive from H-abstraction and addition reactions involving CP, the cyclopentenyl radical, BNEN, and radical **3** (see Scheme I). A fifth BNEN–CP adduct presumably arises by an H-abstraction reaction involving the carbonyl oxygen atom of a BNEN n,π* triplet (see below). Although a BNEN–cyclopentene [2 + 2] cycloadduct was not isolated, the presence of a trace quantity of such a product in the reaction mixture cannot be unequivocally ruled out. Upon prolonged irradiation in acetonitrile, BNEN proved to be essentially photostable; traces of products of reductive dimerization (*m/e* 274) were the only products that could be detected by GC/MS. Despite the high rate constant for quenching by FN, irradiation of BNEN in the presence of this alkene in acetonitrile did not yield any [2 + 2] cycloadducts. Photorearrangement of BNEN did not occur under any of these conditions, which is not surprising given the absence of substituents at C-5.[4] Unlike its 5,5-dimethyl analog **1**,[6] BNEN was found to be photostable in *tert*-butyl alcohol.

Scheme II



Irradiation of BNEN in 2-propanol afforded *cis*- and *trans*-**6** in the same ratio (4:1) as in cyclopentene. In addition to these compounds, a product concluded to be allylic alcohol **8** is also observed as a primary photoproduct, though in low yield (ratio **8**:(*cis*-**6** + *trans*-**6**), 0.06). The identity of this compound was established by its independent synthesis by reduction of BNEN with sodium borohydride in the presence of cerium trichloride.[19] Compound **8** would arise most reasonably by an H-abstraction reaction involving the carbonyl oxygen of an n,π* triplet state of BNEN (Scheme II), suggesting that the (π,π*) and (n,π*) triplet states of BNEN are very close in energy in 2-propanol. Reduction of *cis*- and *trans*-**6** to alcohols of type **9** (mixture of stereoisomers) presumably via n,π* triplets (Scheme II) constitutes a major, secondary photoprocess in this solvent. The very high triplet energy of BNEN measured by PAC is compatible with close-lying n,π* and π,π* states in this system, even in polar solvents, since stabilization of the π,π* triplet by twisting around the C=C bond, as in other cyclohexenones,[2,5] is simply not possible in the case

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of BNEN. The tendency of BNEN to undergo H-abstraction to yield radical **3** is compatible with the hypothesis that the β-carbon of BNEN is distorted toward a pyramidal geometry in its (π,π^*) triplet state.

Conclusions

The photophysical and photochemical properties of BNEN differ drastically from those of flexible cyclic enones and are in accord with its exceptional conformational rigidity. Thus, both the lifetime and the energy of the BNEN triplet exceed those of most other enones, including cyclopentenone. Thus, it is not surprising that n,π^* and π,π^* states are close in energy in this system, whereas conformationally flexible cyclohexenones tend to have lowest π,π^* triplet states.[1d] This suggestion is supported by the photochemical reactions of BNEN, which are atypical of cyclohexenones. Thus, fumaro- and maleonitrile quench the BNEN triplet by energy transfer, at a diffusion-controlled rate, whereas other cyclohexenone triplets are generally quenched by these alkenes by a Schenck-like addition mechanism.[3] The quenching of BNEN triplets by FN and MN leads exclusively to cis-trans isomerization and not to formation of [2 + 2] cycloadducts, as found with other cyclohexenones.[1] Triplet self-quenching could involve formation of dimeric triplet 1,4-biradicals, even though [2 + 2] photodimers are not formed, as well as intermolecular hydrogen abstraction. The large solvent effects on the limiting triplet lifetime and on the rate constants for self-quenching and for quenching of the BNEN triplet by $^3O_2$ indicate that the T_1 state of BNEN has greater π,π^* character in acetonitrile than in benzene; it is not inconceivable that the n,π^* triplet is in fact the lowest triplet in both of these solvents. Consistent with its photophysical properties, the photochemistry of BNEN is dominated by H-abstraction reactions; BNEN undergoes neither [2 + 2] photocycloaddition reactions nor the lumiketone rearrangement. The formation of photoproducts in 2-propanol deriving from H-abstraction reactions involving both the carbonyl group and the C=C bond (Scheme II) further indicates that in this solvent the (n,π^*) and (π,π^*) triplet states of BNEN are very close in energy.

Experimental Section

General Methods. GC analyses were performed with an HP Model 5890 GC, equipped with a 30 m × 0.25 mm Alltech Heliflex RSL-150 capillary column, and operated isothermally at 130 °C. Mass spectra were taken on HP 5992B and 8992 II GCMS systems. The HP 8992 II MS system was coupled to a HP 5890 GC system. For both EI (70 eV) and CI (CH_4 or NH_3) MS, the instrument was calibrated with $(n\text{-}C_4F_9)_3N$. ^1H (300 MHz) and ^{13}C (75.48 MHz) NMR spectra were recorded on a General Electric QE-300 spectrometer, using TMS as the internal standard.

Materials. Solvents and reagents were obtained commercially and used as received, unless noted otherwise.

Bicyclo[4.3.0]non-1(6)-en-2-one (BNEN, 2) was prepared according to the sequence described by Cram.[20] For the first reaction in the sequence, i.e., the reductive dimerization of cyclopentanone to 1,1′-bicyclopentane-1,1′-diol with aluminum amalgam, the improved method of Schreibmann[21] was employed. The crude BNEN was distilled under vacuum, using a B/R 24 T Teflon-banded, adiabatic still (50 theoretical plates). The band was spun at 6000 rpm, and pure (>99.9%, GC) BNEN, bp 90–91 °C/13 mm, was collected at a rate of ca. 2 mL/h. Under our GC conditions, this material appeared as a single peak with retention time 2.96_5 min. The ^1H NMR spectrum in $CDCl_3$ showed multiplets centered at 1.74, 1.88, 2.20, and 2.40 ppm and no resonances for vinyl protons. ^{13}C NMR: 197.45 (C-2), 165.39 (C-1), 137.18 (C-6), 37.29, 37.38, 28.69, 28.24, 23.11, and 21.13 ppm.

Fumaronitrile was recrystallized from absolute ethanol (5 mL g^{-1}) prior to use. Maleonitrile was prepared by triplet-sensitized, photochemical cis-trans isomerization of fumaronitrile in acetonitrile;[11] the final product, isolated by distillation under vacuum using a spinning band still, was 99.9% (GC) pure.

Nanosecond Transient Absorption Spectroscopy. The equipment used for nanosecond transient absorption spectroscopy and details regarding the analysis of the kinetic data are described in previous papers.[2,8] This technique was used to measure the transient absorption spectra of the BNEN triplet and of the radicals generated by self-quenching of this triplet, as well as the rate constants for quenching of the BNEN triplet by ground-state BNEN (self-quenching), fumaronitrile, maleonitrile, cyclohexane, and $^3O_2$ (Figures 1–4, Table I). In the latter experiment, the oxygen concentration was varied by bubbling O_2–N_2 mixtures with different O_2:N_2 ratios through the sample. The oxygen concentrations were derived from standard solubility tables.[22]

Quantum yields of $^1O_2$ formation from BNEN and $k_q^{O_2}\tau_T$ values for quenching of the BNEN triplet by $^3O_2$ were evaluated by monitoring the intensity of the $^1O_2$ phosphorescence at 1250 nm.[13] The agreement between the sets of τ_T-values (Table I) evaluated by this technique and by nanosecond transient absorption spectroscopy is satisfactory.

Photoacoustic Calorimetry. The triplet energy (E_T) of BNEN was determined by two complementary photoacoustic calorimetry techniques. The experiments utilized a photoacoustic cell designed by Melton,[23a] an excitation wavelength of 337 nm, 0.12 M BNEN corresponding to OD_{337} = 5.21 cm^{-1} in acetonitrile, and deconvolution of the photoacoustic wave from the BNEN sample against that from an *o*-hydroxybenzophenone calibration reference.[23] It was found that E_T = 74 ± 2 kcal mol^{-1}, in accord with an earlier result.[5] Under these conditions ca. 40% of the excitation energy is returned as heat within the 2-μs observation window of this technique. The remainder of the excitation energy is presumably stored in the long-lived radicals (τ = 4.1 μs) generated by self-quenching of the BNEN triplet. Using Braslavsky's method,[24] with much lower BNEN concentrations ((2–5) × 10^{-3} M, corresponding to an OD of ca. 0.1 cm^{-1} at 308 nm) in acetonitrile, and benzophenone–KI (8 × 10^{-3} M) as the photoacoustic reference, E_T was determined to be 76 ± 7 kcal mol^{-1}, which is identical within experimental error to the value obtained above at high BNEN concentrations. Avoiding self-quenching by utilizing low concentrations of BNEN, Braslavsky's method gave a triplet lifetime τ_T of (0.9 ± 0.3) μs, which is in fair agreement with the limiting lifetime (τ_T = 1.4 μs) obtained from transient absorption spectroscopy.

Irradiations of BNEN and Characterization of the Reaction Products. A degassed solution of BNEN (0.05 M) in cyclopentene (25 mL) was irradiated through Pyrex at 300 nm. Samples, taken after 1, 6.5, and 18 h, were analyzed by GC/MS. From EI and CI GC/MS analyses of samples irradiated for 1 and 6.5 h, 1,1′-bi-2-cyclopentenyl (**5**, *m/e* 134), *cis*- and *trans*-bicyclo[4.3.0]nonan-2-one (**6**, *cis*:*trans* ratio, 4:1), and five 1:1 BNEN–cyclopentene adducts (*m/e* 204) were found to be primary photoproducts of the reaction. The formation of secondary photoproducts set in at very low BNEN conversion (>5%). EI and CI GC/MS analyses of a BNEN sample irradiated for 18 h revealed the formation of isomeric alcohols of type **9**, six additional 1:1 BNEN–cyclopentene adducts (*m/e* 204), and at least four 2:1 BNEN–cyclopentene adducts (*m/e* 272) as secondary photoproducts. The irradiations of BNEN in 2-propanol were performed under similar conditions. GC/MS analyses revealed the presence of *cis*-**6**, *trans*-**6** (ratio: 4:1), and a new product identified as **8** (see below) as the primary photoproducts, and **9** as the major secondary photoproduct of the reaction.

Of these photoproducts, 1,1′-bi-2-cyclopentenyl (**5**) was recognized by its mass spectrum,[25] which displays a molecular ion peak at *m/z* 134 (4%) and major fragmentation peaks at *m/z* 67 (100%) and 66 (59%). The compounds *cis*-**6**, *trans*-**6**, **8**, and **9** were characterized by independent chemical synthesis, as described below.

***cis*-Bicyclo[4.3.0]nonan-2-one (*cis*-6).** This compound was prepared in quantitative yield and 98% purity by shaking a solution of BNEN (400 mg) in ethyl acetate (30 mL) with 10% Pd/C (100 mg) under H_2 (p = 4.8 bar) for 3 days. ^1H NMR ($CDCl_3$): δ 2.58 (m, 1 H, H1), 2.48–1.30 (m, 13 H). ^{13}C NMR ($CDCl_3$): δ 214.53 (C-2), 53.12 (C-1), 42.95 (C-6), 39.60 (C-3), 30.90 (C-5), 27.25, 26.64, 23.83, 23.07. EIMS (70 eV), *m/z* (rel intensity): 138 (M^+, 16), 110 ($M^+ - CO$, 18), 97 (80), 95 (30), 94 (23), 82 (11), 81 (14), 80 (10), 79 (33), 68 (18), 67 (100). CIMS (CH_4), *m/z* (rel intensity): 139 ($M^+ + 1$, 57), 121 ($M^+ - H_2O$, 100).

***trans*-Bicyclo[4.3.0]nonan-2-one (*trans*-6).** This compound was prepared by base-catalyzed epimerization of the cis isomer (100 mg) with 10% NaOH in methanol–water, 1:1 v/v, at 60 °C for 24 h. The solvent was evaporated and the residue extracted with diethyl ether (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and filtered. GC analysis

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of the filtrate revealed it to contain *cis*- and *trans*-**6** in a ratio of 85:15, which could not be improved by extending the reaction time or performing the epimerization reaction with sodium methoxide in methanol. Following evaporation of the solvent, the 85:15 mixture was enriched in the trans isomer by column chromatography using Merck 60 silica gel and cyclohexane–diethyl ether, 9:1 v/v, as the eluant. The fraction most enriched in *trans*-**6** contained *cis*- and *trans*-**6** in a 1:1 ratio; further enrichment proved to be impossible because silica gel catalyzes the epimerization of *trans*-**6** into its cis isomer. From the ^{13}C NMR spectra ($CDCl_3$) of pure *cis*-**6** and of the 1:1 mixture of the cis and trans isomers, the following resonances could be assigned to *trans*-**6**: 211.93 (C-2), 58.06 (C-1), 49.64 (C-6), 41.46 (C-3), 32.22, 30.79, 27.91, 22.50, 21.45. EIMS (70 eV), m/z (rel intensity): 138 (M^+, 11), 110 ($M^+ - CO$, 7), 97 (12), 96 (13), 95 (100), 82 (7), 81 (11), 80 (5), 79 (20), 68 (15), 67 (71). CIMS (CH_4), m/z (rel intensity): 139 ($M^+ + 1$, 62), 121 ($M^+ - H_2O$, 100).

Bicyclo[4.3.0]non-1(6)-en-2-ol (8). This compound was prepared by reduction of BNEN according to the method of Luche.[19] BNEN (136 mg, 1 mmol) was dissolved in 2.5 mL of a methanol solution of 0.4 M $CeCl_3{\cdot}7H_2O$. To this was slowly added 1 mmol of $NaBH_4$ over a 2-min period with constant stirring. The mixture was allowed to react at room temperature for 20 min, followed by addition of water and extraction with ether. The ether extracts, after being dried over sodium sulfate, were concentrated to give a yellow oil, which was purified on a silica gel column using 10:1 petroleum ether–diethyl ether as the eluant. The resulting material gave only a single peak at 2.72 min on GC analysis under our standard set of conditions. Coinjection with a sample of the 2-propanol photolysate of BNEN on the GC capillary column showed enhancement of the product peak present at 2.718 min relative to that of residual BNEN at 2.975 min. On GC/MS analysis, allylic alcohol **8** showed major peaks at 138 (M^+, 33), 120 ($M^+ - H_2O$, 19), 110 ($M^+ - C_2H_4$, 100), 95 (75), 92 (36) 91 (67), 79 (60), 77 (37), 67 (64), 66 (33), and 41 (58). The CI (CH_4) mass spectrum of **8** exhibits a weak parent peak at the correct mass (m/z 139 ($M^+ + 1$, 6)) and an intense peak at m/z 121 ($M^+ - H_2O$, 100), but lacks the fragmentation peak at m/z 110 ($M^+ - 28$). The EIMS spectrum of **8** shows m/z (rel intensity) 120 ($M^+ - H_2O$, 22), 94 (37), 91 (12), 81 (13), 80 (12), 79 (100), 77 (14), 67 (55). ^{13}C NMR ($CDCl_3$): 139.87 (C-1), 136.10 (C-6), 66.48 (C-2), 36.48 (C-3), 33.05 (C-9), 32.85 (C-7), 26.17 (C-5), 22.00 (C-4), and 19.60 (C-8). ^1H NMR ($CDCl_3$): 4.15 (br s, C*H*OH), and unresolved multiplets at 2.5, 2.3, and 1.0–2.0 ppm.

(*Z*-(1,6))-Bicyclo[4.3.0]nonan-2-ol (9). Compound **9** was prepared by exhaustive hydrogenation ($p(H_2) = 4.8$ bar, 5 days) of a solution of BNEN (200 mg) in ethyl acetate with 100 mg of Adams' catalyst (hydrated PtO_2). After evaporation of the solvent, the crude product was separated from **6** by column chromatography. This afforded 45 mg of pure **9**. ^1H NMR ($CDCl_3$): δ 3.94 (m, 1 H, H2), 2.22 (m, 1 H, H1), 1.93 (m, 1 H, H6), 1.75–0.89 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ 71.49 (C-2), 46.34 (C-1), 40.10 (C-6), 31.52, 29.43, 27.04, 23.94, 21.35, 21.05. CIMS (NH_3), m/z (rel intensity): 157 ($M^+ + NH_3$, 1), 141 (M^+, 2), 140 (1), 139 (8), 124 (10), 123 ($M^+ - H_2O$, 100), 121 (25).

BNEN–Cyclopentene Adducts. The stoichiometries of the 1:1 and 2:1 BNEN–cyclopentene adducts were inferred from their CI and EIMS spectra. The EI and CIMS spectra of the 1:1 and 1:2 BNEN–cyclopentene adducts display molecular ion peaks at the correct mass and strong peaks due to fragmentation of one or both cyclopentenyl groups from the parent ion.

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Carbene Formation, Hydrogen Migration, and Fluorescence in the Excited States of Dialkyldiazirines†

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Abstract: Photolysis of 3,3-dimethyldiazirine produces an electronically excited singlet state which decays by at least three competitive pathways: (1) fluorescence, (2) nitrogen extrusion and carbene formation, and (3) α-hydrogen migration and propylene formation concurrent with nitrogen extrusion. The temperature dependence of the fluorescence intensity was determined.

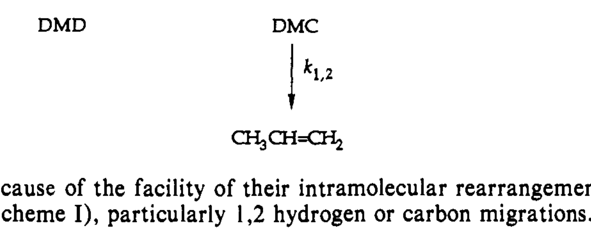
I. Introduction

Methylene (CH_2) is by now a rather well-understood compound.[1] The geometries of singlet and triplet CH_2 have been determined by gas-phase spectroscopy, and the singlet–triplet energy separation between these states has been determined experimentally.[2]

The intermolecular chemistry of $^1CH_2$ and $^3CH_2$ in the gas phase and in solution is also well documented.[3] The reactions of methylene in solution have been studied by CIDNP spectroscopy,[4] and Turro has analyzed the dynamics of these processes using nanosecond laser flash photolysis techniques.[5]

Progress in the study of alkylcarbenes and dialkylcarbenes has evolved more slowly. It is difficult to intercept dialkylcarbenes with chemical traps in better than very low yields presumably because of the facility of their intramolecular rearrangements (Scheme I), particularly 1,2 hydrogen or carbon migrations.[3,6]

Scheme I



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† This paper is dedicated to the memory of Professor Gerhard L. Closs.

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