

Triplet Species from Norbornadiene. Time-Resolved Photoacoustic Calorimetry and *ab Initio* Studies of Energy, Geometry, and Spin–Orbit Coupling

Anna M. Helms and Richard A. Caldwell*

Contribution from the Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75083

Received September 27, 1993[⊗]

Abstract: The norbornadiene triplet is directly observed and its energy measured for the first time by time-resolved photoacoustic calorimetry. PAC affords a transient subsequent to the sensitizer triplet, with a lifetime of 6.20 ± 0.03 ns and an energy of 61.37 ± 0.25 kcal/mol relative to ND, which we have ascribed to the norbornadiene triplet. The lifetime of the triplet, which is anomalously short, is determined by the rate at which the species undergoes rearrangement along the path to quadricyclane. Calculations for the norbornene triplet indicate that its short lifetime is consistent with $T_1 \rightarrow S_0$ intersystem crossing.

The valence isomerization of norbornadiene (ND) to quadricyclane (Q) occurs with unit quantum yield when photosensitized with acetophenone.¹ The reaction has been suggested as a potential method for storage of solar energy because of the high latent heat (22 kcal/mol)² of the ND \rightarrow Q isomerization coupled with the kinetic stability of Q.³ Recent work has also shown that norbornadiene can be considered a molecular switch as it fulfills three of the four requirements proposed by Haddon and Lamola⁴ for an operational molecular switch.⁵ Scheme 1 illustrates the triplet state intermediates, which include at a minimum the norbornadiene triplet, ³ND, and the 3,5-nortricyclyl diradical, ³D. While they have been approached experimentally⁶ and theoretically,⁷ neither ³ND nor ³D has ever been detected. The most likely reason for this is the probable inaccessibility of either ³ND or ³D by optically detected laser flash photolysis. Our recent development of methodology which permits time-resolved photoacoustic calorimetry (PAC) in the 5–10 ns time regime, however, permits detection of even such a short-lived species provided its heat content differs significantly from the ground state, as would ³ND and ³D.⁸ Accordingly, we have studied the photosensitized ND \rightarrow Q isomerization by PAC, in addition to conventional laser flash photolysis and *ab initio* calculations. We compare the properties of ³ND to those of the norbornene triplet, 3NE, and also offer an explanation for the anomalous lifetime for the latter.

Experimental Section

Materials. Spectroscopic grade solvents were used as received. 2-hydroxybenzophenone, ferrocene, and *p*-methoxyacetophenone were

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

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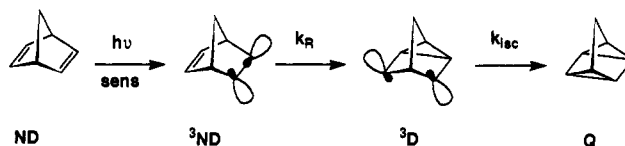
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Scheme 1



recrystallized twice from appropriate solvents. Norbornadiene, norbornene, and acetophenone were distilled prior to use.

Kinetic Absorption Spectroscopy. Quenching rate constants were determined by laser flash photolysis through standard techniques.⁹

Singlet Oxygen Measurements. Following the methods outlined by Gorman and Rodgers,¹⁰ $O_2^1\Delta_g$ lifetimes were measured through the direct detection of the 1269 nm luminescence. The S_Δ values were obtained by using naphthalene as a reference compound. Gorman *et al.* have shown previously that in cyclohexane solution S_Δ for naphthalene, when sensitized by aromatic ketones at 355 nm, is equal to 1.11. *p*-Methoxyacetophenone was used to sensitize cyclohexane solutions of naphthalene and norbornadiene over a concentration range of 0 to 0.5 M. The absorbances of these solutions at 355 nm were matched. Measurements were made in N_2 -sparged solution, air-saturated solution, and oxygen-saturated solution.

Photoacoustic Measurements. The photoacoustic apparatus has been described previously.⁸ Briefly, PAC measurements were made using a front face irradiation cell with 266 and 355 nm excitation provided by a Continuum Model YG671-C-10 Nd-YAG laser (Q-switched) and 337 nm excitation provided by a Lumonics TE 860 series laser. Data were acquired at 2 Hz. The optical density of the T-wave was matched to that of the E-wave with typical absorbances ranging from 5 to 7 cm^{-1} . Each measurement consisted of 100 averaged shots. Data analysis procedures have also been described previously.¹² In general, six-parameter fits (three heat functions, ϕ_{1-3} , and three time functions, τ_{1-3}) with three of the six parameters fixed were employed. ϕ_1 and τ_1 are known properties of the sensitizer: The value of ϕ_1 is fixed based upon the triplet energy of the sensitizer which is either known or can be measured through a separate PAC experiment; τ_1 is fixed at 0.1 ns since the intersystem crossing rate of the sensitizer is

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Table 1. Quenching Rate Constants

quencher	sensitizer (E_T , kcal/mol)	solvent	k_Q ($M^{-1} s^{-1}$)
norbornadiene	<i>p</i> -methoxyacetophenone (72.4)	methanol	4.8×10^9
	acetophenone (73.7)	cyclohexane	8.3×10^9
norbornene	acetone (78)	cyclohexane	6.8×10^9
	<i>p</i> -methoxyacetophenone (72.4)	acetone	1.9×10^7
oxygen	<i>p</i> -methoxyacetophenone (72.4)	heptane	3.2×10^7
	<i>p</i> -methoxyacetophenone (72.4)	cyclohexane	5.9×10^9

faster than the transducer can resolve. τ_2 is derived from the measured quenching rate constant: $\tau_2 = (k_Q[Q])^{-1}$. The norbornadiene data were also subjected to further analysis by an eight-parameter fit in an effort to observe both anticipated intermediates, 3ND and 3D . Both 2-hydroxybenzophenone and ferrocene were used as calibration compounds. Data were collected at 337 and 355 nm dependent upon sensitizer and calibration compound. *p*-Methoxyacetophenone and acetophenone were used as triplet sensitizers in both cyclohexane and methanol. Norbornadiene is transparent at both of these wavelengths at experimental concentrations. Data were collected with either a 10 MHz transducer (Panametrics A611S-SB) with a 25 μm shim or a 3.5 MHz transducer (Panametrics A682S-RB) with a 100 μm shim.

Results and Discussion

The quenching of sensitizer triplets by ND in either cyclohexane or methanol, studied by KAS, afforded linear plots of the observed pseudo-first-order decay rate constant against ND (Table 1). The experimental quenching rate constants are all within the diffusion-controlled limit as would be expected of a species with an energy in the low to mid 60 kcal/mol range. An optical search led to the detection of no transients other than those assigned to the sensitizers in the KAS experiments. This result led to the pursuit of PAC experiments, since PAC does not require an optically detectable species.

In all cases, PAC affords a transient subsequent to the sensitizer triplet, with a lifetime of 6.20 ± 0.03 ns and an energy of 61.37 ± 0.25 kcal/mol relative to ND.¹³ These values were consistent under various conditions of incident laser powers, ranging from 4 to 0.5 mJ/pulse, and ND concentrations, ranging from 0.05 to 0.2 M. The distinction between 3ND and 3D rests on our observation of $O_2(^1\Delta_g)$ luminescence sensitized by 3ND with $S_\Delta = 0.08$. Since the diradical 3D is expected to have a vertical $T_1 \rightarrow S_0$ gap much less than the 22.5 kcal/mol required to produce $O_2(^1\Delta_g)$ exothermically from ground state dioxygen, we would have expected a negligible S_Δ if 3D were the intermediate and accordingly assign the intermediate as 3ND . An oxygen-saturated PAC experiment in cyclohexane with 0.1 M ND yielded the same triplet energy for norbornadiene and a lifetime shortened to 3.73 ± 0.12 ns. To our knowledge, this is the fastest lifetime yet to be reported from a PAC experiment. A representative PAC trace is shown in Figure 1. The residual heat of 23.24 ± 0.18 kcal/mol after 3ND decay is in excellent agreement with the known $D \rightarrow Q$ latent heat of 22 kcal/mol.²

The lifetime of 3D is unknown. Simulations with 3D lifetimes in the 1–6 ns regime have yielded no significant deviation from the initial PAC results. The computational results for 3D show high SOC and a small vertical $T_1 \rightarrow S_0$ gap, which suggest that 3D undergoes ISC very rapidly, probably faster than 1 ns.

Computations of Geometry, Energy, and Spin–Orbit Coupling. The species ND, NE, and D are all critical to the understanding of our observations and we have examined each computationally. In order to maintain as close a comparison as possible to our earlier work on SOC,¹⁴ we have retained the

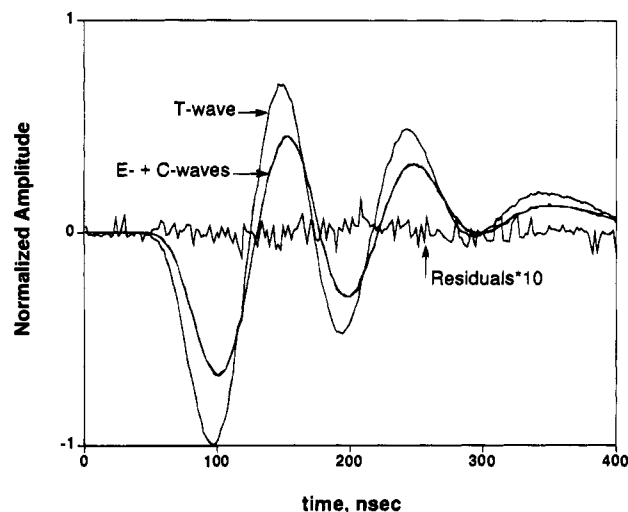


Figure 1. A representative photoacoustic waveform: norbornadiene. The amplitude of the T-wave (2-hydroxybenzophenone) is normalized; the C- and E-waves (0.1 M norbornadiene, *p*-methoxyacetophenone) are shown to the same scale; residuals are shown amplified by a factor of 10. The solvent is cyclohexane.

Table 2. Calculated Properties for 3NE , 3ND , and 3D

hydrogens	E_T , ^a kcal/mol	vertical E_T , kcal/mol	$T_1 - S_0$ SOCC, cm^{-1}
3NE			
exo, exo	70.89	31.04	2.038
exo, endo	67.84	19.65	1.023
endo, endo	71.08	37.68	2.413
3ND			
exo, exo	64.51	29.75	2.037
exo, endo	63.30	20.66	0.845
endo, endo	66.30	30.13	1.843
3D			
exo, exo	62.90	-1.41	0.095
exo, endo	62.38	-1.94	0.190
endo, endo	62.50	-0.96	0.671

^a Relative to the fully optimized 2-in-2 CAS singlet ground state of NE or ND as appropriate.

use of a 3-21G basis set and 2-in-2 CAS-MCSCF calculations. We do not expect that the results we present below would be substantially different were a larger basis set or active space used.

The structures of all three species were optimized. No Hessian calculations were done since the structural results for 3NE closely paralleled those of Houk *et al.*¹⁵ For each triplet, 3NE , 3ND , and 3D , three separate minima were located. They correspond to the three stereochemical placements of the vinyl hydrogens for 3NE and 3ND or the hydrogens at the radical-like termini for 3D . The hydrogens can be either exo (x) or endo (n) in the bicyclic system and xx, xn, and nn are geometric isomers. The structures xn and nx are enantiomeric and only one needed to be explored.

Table 2 shows the energies of the three minima for each of the three triplet species, both relative to the calculated energy of the optimized ground state and relative to the S_0 structure held at the geometry of the triplet species. Although our SOC calculations use the frozen core approximation for the singlet, in the structure optimization the core was not frozen. The frozen

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(13) Errors are reported at the 90% confidence level. Note that this is an indication of precision and that the absolute error in ΔH is expected to be larger.

Table 3. Essential Features of the Optimized Geometries of ³ND, ND, D, ³NE, and NE^a

feature ^b	³ N D _{nn}	³ N D _{xn}	³ N D _{xx}	N D _{op}	³ D _{nn}	³ D _{xn}	³ D _{xx}	³ N E _{nn}	³ N E _{xn}	³ N E _{xx}	N E _{op}
R(3-4), Å	1.566	1.535	1.566	1.320	1.495	1.500	1.500	1.571	1.529	1.564	1.344
R(5-6), Å	1.326	1.324	1.323	1.342	1.495	1.500	1.500	1.573	1.572	1.572	1.571
R(3-6), Å	2.409	2.395	2.426	2.477	1.567	1.549	1.537	2.473	2.501	2.481	2.466
R(1-4), Å	1.540	1.540	1.539	1.548	1.537	1.536	1.529	1.524	1.529	1.525	1.532
R(1-5), Å	1.536	1.535	1.536	1.551	1.537	1.529	1.530	1.557	1.558	1.555	1.565
R(3-8), Å	1.076	1.076	1.077	1.069	1.067	1.068	1.067	1.077	1.079	1.079	1.070
R(4-9), Å	1.076	1.077	1.077	1.069	1.072	1.073	1.073	1.077	1.076	1.075	1.070
A(1-4-3), deg	103.43	103.76	103.46	107.58	99.87	99.91	99.91	103.71	104.66	104.31	107.56
A(2-3-4), deg	103.44	103.92	103.47	107.59	106.05	106.03	105.87	103.58	103.63	103.34	107.56
A(1-5-6), deg	108.12	108.28	108.20	107.12	99.86	99.93	99.89	103.20	102.94	103.20	102.86
A(2-6-5), deg	108.12	108.00	108.22	107.12	106.06	105.88	105.89	103.39	103.74	103.68	102.87
A(1-7-2), deg	94.35	94.02	94.12	92.29	97.09	97.13	97.14	95.05	94.85	95.09	93.89
D(9-4-3-1), deg	136.51	-132.62 ^x	-135.95	177.62	141.21	-142.05 ^x	-140.97	134.97	135.99 ^x	-141.87	173.88
D(8-3-4-2), deg	-136.41	-134.83 ⁿ	135.95	-177.62	150.98	149.85	149.21	-137.25	131.01 ^x	132.40	-173.89
D(8-3-4-9), deg	0.00	99.78	0.00	0.00	-36.96	38.36	39.94	-4.03	-104.02	-15.18	0.00
D(10-5-6-1), deg	-174.69	-175.58	-174.58	-177.02	-141.20	-140.31 ⁿ	140.62	-120.55	-120.76	-120.49	-120.21
D(11-6-5-2), deg	174.69	174.80	174.58	177.02	150.98	-149.93	-149.21	120.23	119.87	119.67	120.21
D(1-4-3-2), deg	0.00	7.24	0.00	0.00	30.86	30.56	31.70	-1.76	-11.01	-5.72	0.00

^a Structures with left superscript 3 are triplet species; others are ground state. Structure abbreviations as in text; subscripts to structures refer to orientation (exo or endo) of hydrogens 8 and 9 for ³NE and ³ND and of hydrogens 9 and 10 for ³D. Subscript n refers to endo hydrogen and subscript x refers to exo hydrogen. ^b R = interatomic distance, Å; A = bond angle, deg; D = dihedral angle, deg. Atom numbers refer to Figure 2.

core singlets were each about 1.2 kcal/mol above the optimized species and the two had identical geometries. For ³ND and ³D the reference ground state structure was taken as ND since that was the reactant in the PAC studies. For ³NE the ground state was simply NE. Table 2 also shows the T₁-S₀ spin-orbit coupling obtained for each optimized triplet species. No spin-orbit surface was studied in view of the relatively long time required for calculation of C₇ structures. As the minima all were at positions at which SOC was substantial for hydrocarbon structures, *cf.* compared to that at the minimum D_{2d} structure for ethylene, geometric excursions away from the minima may not be particularly relevant to ISC in these species. Table 3 lists the essential features of the computed geometries.

For ³ND, the optimized structures clearly have one ordinary and one excited double bond, and not a C_{2v} structure, in agreement with the earlier results of Haddon.⁷ A bond length slightly over 1.32 Å, found for the "unexcited" C5-C6 double bond, is a normal C=C bond length. The "excited" double bond, C3-C4, has a length of 1.566 Å for both the xx and nn isomers, even longer than the ordinary 1.54 Å for a C-C single bond. For the xn isomer, the C3-C4 bond length of 1.535 Å is still long for a supposed sp²-sp² single bond distance, usually about 1.48 Å, but is shorter than that for the xx and nn isomers. Also, for ³ND, the exo, endo structure is clearly the lowest in energy. We suggest that both the energies of the triplet isomers and in part the trend of C3-C4 bond lengths arise from the repulsion of the unpaired electrons for each structure: in the xx and nn structures the axes of the orbitals containing them are coplanar, which enforces the maximum electrostatic interaction between them, albeit presumably not as much as would be the case were pyramidalization prohibited. However, in the xn isomer, the orbitals containing the unpaired electrons must be close to orthogonal. The dihedral angles H8-C3-C4-C2 and H9-C4-C3-C1 roughly measure the pyramidalization at C3 and C4 respectively,¹¹ with values of 180° and 120° corresponding respectively to sp² and sp³ hybridization of perfectly trigonal and tetrahedral carbons. The magnitudes of the values for xx, xn, and nn triplets are 132.62-136.51°, actually nearer to those expected for sp³ than for sp² hybridization. A slight pyramidalization for the "unexcited" C=C double bond, *cf.* the analogous dihedral angles of 174.6-177.0°, found in the present work for all three triplets and the ground state, is in line with expectation.¹⁵

Results for ³D show pyramidalizations at both radical termini, with H9-C4-C3-C1 and H10-C5-C6-C1 dihedral angles of 140.3° to 142.1°. These values are farther from sp³ than those for ³ND but still closer to sp³ than sp². The energy differences between isomeric triplets are smaller than for ³ND, as would be expected for a 1,3-biradical considering its greater distance between the termini.

Results for ³NE are fully consonant with expectations based on ³ND. The extents of pyramidalization at the vinyl carbons in the triplets are slightly more variable. The C5-C6 bond lengths in the triplets exceed 1.57 Å, quite long for a C-C single bond, presumably because the extension better accommodates the ring strain inherent in the bicyclic system. The same effect may contribute as well as repulsion of the unpaired electrons to the C3-C4 distance.

For ³ND, the computed values of 63-66 kcal/mol are somewhat higher than experiment. We regard it as a substantial success for the computational protocol, however, that the agreement in E_T between calculation and experiment is as good as it is.

At What Geometries Does Intersystem Crossing Occur?

We expect this to result from a balance between the energy of the species, the T₁-S₀ spin-orbit coupling and the T₁-S₀ energy gap at each geometry. As the SOC values are all large and comparable at each structure for ³NE and ³ND, energy factors seem likely to be the major consideration. In this regard there is a clear preference for the xn geometries. In each triplet, as stated above, these structures minimize both the T₁ energy and the T₁-S₀ energy gap. The xn structures are shown in Figure 2. In the xn geometries the H8-C3-C4-H9 dihedral angles of ³ND and ³NE, 99.78° and 104.02°, respectively, actually exceed the 90° of the twisted triplet of ethylene! The carbon skeleton of the alkene remains essentially planar (C1-C4-C3-C2 dihedral angles of 0-11°). The minimization of overlap of the hybrid orbitals not only minimizes the repulsions of the electrons in those orbitals in the triplet but also provides the least bonding in the ground state, and thus leads to minimization of the T₁-S₀ energy gap. The short lifetime of the norbornene triplet, instead of being an anomaly, is in fact well rationalized by the pyramidalization of the vinyl carbons in the optimized structure.

Many years ago, Arnold and Abraitys¹⁶ discussed the dimerization of norbornene on the basis of postulated pyramidal vinyl

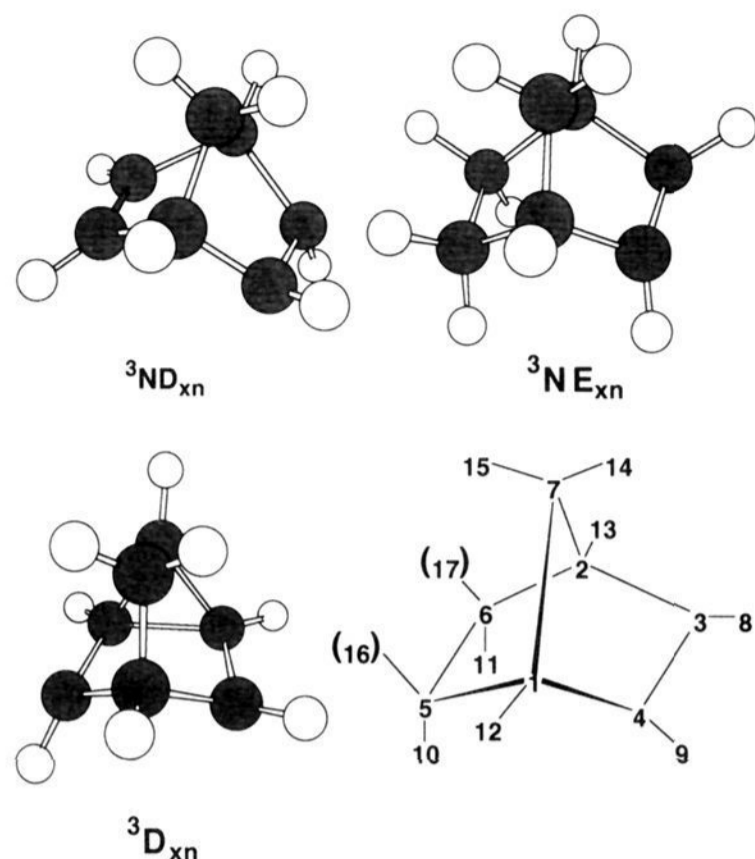


Figure 2. Structures of preferred geometries of triplet species and the atom numbering scheme used throughout this paper. Atoms 16 and 17 are relevant only for NE and ^3NE .

carbons for the triplet. At that time the exo, endo mode of pyramidalization was not explicitly considered. In light of the present results, we suggest that the favored structure may also be the precursor of both the norbornene photodimers.

The NE triplet has been detected in pulse radiolysis by excitation transfer with a lifetime of 250 ns.¹⁷ The 40-fold difference in lifetimes between ^3NE and ^3ND cannot be ascribed to differences in the intersystem crossing (isc) rates since the differences in SOC between ^3ND and ^3NE suggest only a small difference in isc rate. However, if $T_1 \rightarrow S_0$ isc were similar in the two, at *ca.* $3\text{--}4 \times 10^6 \text{ s}^{-1}$, and the short lifetimes for ^3ND assigned to the rapid $^3\text{ND} \rightarrow ^3\text{D}$ rearrangement, that rearrangement would be some 98% complete and only some 2% of the competing process, $^3\text{ND} \rightarrow \text{ND} + \text{heat}$, could occur. This is exactly what is shown by the high ND \rightarrow Q quantum yield,

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and thus we assign the rate constant of the $^3\text{ND} \rightarrow ^3\text{D}$ rearrangement as $1.6 \times 10^8 \text{ s}^{-1}$.

The isc rate of ^3NE , although the slowest of the cases discussed here, is anomalously fast when compared to presumably planar unsaturated systems, which are invariably long-lived (tens or hundreds of microseconds to seconds), *cf.* aromatic hydrocarbons,¹⁸ arylcyclopentenes,¹⁹ and even 2-phenylnorbornene.¹² The relaxed geometries that we compute show that ^3NE should in no sense be considered a simple planar alkene triplet. The H–C₂–C₃–H dihedral angle is 104.0°, and the C₁–C₂–C₃–C₄ dihedral angle is 11.0°, for the lowest energy exo, endo case. Planarity is approximated only by the carbons; from the view of the hydrogens, the triplet is almost perpendicular, which slightly relaxes the triplet but greatly raises the energy of the ground state. The vertical E_T in Table 2 of 19.65 kcal/mol is accordingly far smaller than would be expected for a planar unconjugated alkene and, when coupled with the substantial SOC, demands rapid isc. A short lifetime for the relatively unconjugated cyclopentenone triplet,²⁰ reported earlier without particular comment, may result from the same phenomenon. Conjugation in our view relieves the electron–electron repulsion responsible for the pyramidalization and thus leads to increased tendency to planarity and to long lifetimes.

The triplet energy of norbornene, as measured by oxygen perturbation, has been reported to be 72.3 kcal/mol.¹² The quenching rate constants listed in Table 1 are much slower than would be expected for a species with this triplet energy. Barwise *et al.* have reported that ^3NE is not quenched by such low-energy triplets as biphenyl ($E_T = 65.7 \text{ kcal/mol}$) and coronene ($E_T = 54.4 \text{ kcal/mol}$).¹⁷ Thus NE neither accepts nor donates energy as would be expected. One possible explanation for this behavior can be found in the calculated structure for ^3NE , which supports Barwise's hypothesis of a distorted triplet. In any case, these observations warrant further study.

Acknowledgment. We thank the National Science Foundation for financial support (Grant Nos. 8820268 and 9121313).

JA933188D

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