Table I. ESR Spectral Data for Diazomethane Radical Cations[a]

diazo compd	g^{b}	a_N,[c] mT	a_H,[d] mT ortho H	 meta H	 CH_3	electronic structure assigned
Ph_2CN_2 (**1**)	2.0009	1.72, 1.01				σ
(p-$MeOC_6H_4)_2CN_2$ (**2**)	2.0012	1.65, 1.02				σ
$Ph(Me)CN_2$ (**3**)	2.0015	1.49, 1.01				σ
p-$MeC_6H_4(t\text{-}Bu)CN_2$ (**4**)	2.0017	0.47,[d] 0.35[d]	0.35 (2H)	0.08 (2H)	0.67 (3H)	π
p-$MeOC_6H_4(t\text{-}Bu)CN_2$ (**5**)	2.0021	0.39,[d] 0.34[d]	0.33 (1H) 0.26 (1H)		0.14 (3H)	π

[a] Generated in an ESR cavity by electrolysis of 20–100 mM diazomethane at 1.2–1.6 V vs. Ag/AgCl in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 at −70 to ca. −90 °C. [b] g value, ±0.0001. [c] Coupling constant, ±0.01 mT (**1–3**). [d] Coupling constant from computer simulation.

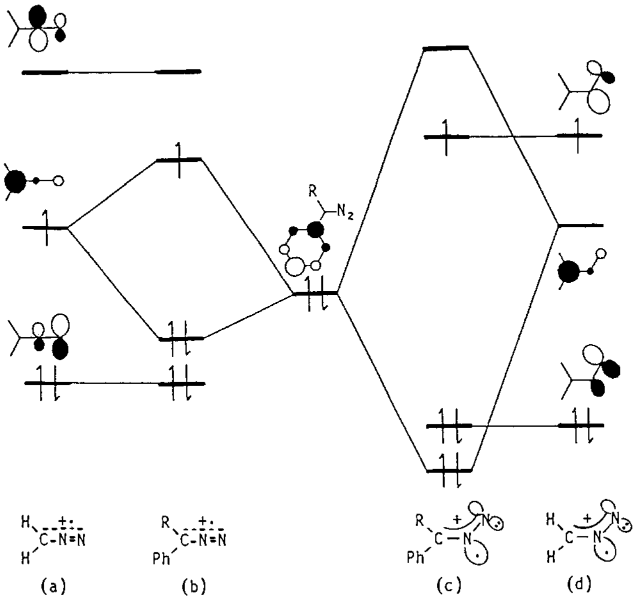

Figure 2. Schematic drawing of MOs of (a) diazomethane linear π-radical cation, (b) *tert*-butylphenyldiazomethane π-radical cation (R = t-Bu), (c) phenyldiazomethane σ-radical cation, and (d) hypothetical diazomethane bent σ-radical cation.

phenyldiazenyl,[7] and nitrosobenzene radical cation,[12] have been reported but without turnover. The present turnover may be analyzed on the basis of MO calculations. Thus, electronic structures for $CH_2N_2^{\bullet+}$ were calculated according to the ab initio UHF-MO method[13] (STO-3G basis).[14] The calculated π-radical cation has a linear C–N–N geometry with a three-centered allylic orbital, which corresponds to the HOMO of CH_2N_2[8] (Figure 2a). On the other hand, the σ-radical cation[15] takes on a planar bent geometry in which an unpaired electron is localized in the in-plane π_{np}*-orbital (Figure 2d). The energy of the optimized σ-radical is 53.7 kcal/mol higher than that of the π-radical. However, the difference for the case of $PhCHN_2^{\bullet+}$ is dramatically reduced down to ~10 kcal/mol. The observed turnover of energy levels seems to be reasonable since the calculated difference is so small and solvation should be significant in solution.

The dramatic effect of phenyl substituent can be well understood as shown in Figure 2. When R = aryl or Me, the energy of the upper C–N–N π-orbital should be significantly raised by interaction with the coplanar phenyl group, resulting in the reversion of the SOMO to the N–N π_{np}*-orbital to afford bent σ-radicals (Figure 2c). But when R = t-Bu, the diazo group is forced by steric repulsion to be twisted out of the phenyl plane, the π-radical structure being retained as observed (Figure 2b). Thus, we have uncovered two contrasting σ and π electronic structures for phenyldiazomethane radical cations.

Further studies on related radical cations are in progress.

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Proton-Transfer Spectroscopy of Benzanilide. The Amide–Imidol Tautomerism

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We report the photoinduced proton-transfer tautomerization of benzanilide (N-phenylbenzamide) to its imidol form (N-phenylbenzimidic acid), structures I and II, Figure 1. The study compares the UV fluorescence (F_1), the violet phosphorescence (P), and a strong blue-green fluorescence (F_2) observed at 293 K in Na-dried, Ar-degassed hydrocarbon solvent. F_2 is identified as the transient fluorescence of the excited imidol tautomer produced by double proton transfer in the H-bonded dimer of *cis*-benzanilide.

The photochemistry of aryl amides and urethanes has generated spectroscopic interest.[1-3] The spectra on one species, benzanilide, if taken at face value, would represent an anomaly to the spectroscopist. For example, the fluorescence maximum reported[4] is 1200 cm^{-1} lower in frequency than the phosphorescence maximum, although the onsets of the singlet–singlet and triplet–singlet emissions seem to be normal in order.

Benzanilide spectra include UV absorption, onset 320 nm, first maximum 265 nm (ϵ 13 000), discrete shoulder 222 nm (10^{-4} M, methylcyclohexane (MCH), 293 K); normal fluorescence F_1, onset 280 nm, maximum 307 nm (10^{-6} M, MCH, 293); and phosphorescence, onset 370 nm, maximum 410 nm (ethanol glass, 77 K). These data generally agree with those published,[4] except that F_1 was not previously observed as a discrete emission; it is very weak and is rapidly replaced by photoproduct emission at slightly longer wavelengths.

The F_2 proton-transfer fluorescence is shown in Figure 2. This luminescence has an onset at 410 nm and maximum at 474 nm at 293 K in MCH. At 77 K the band observed at 444 nm maximum in MCH glass solvent and in ethanol glass at 438 nm and at[4] 435 nm for EPA at 77 K represents a total emission: $P + F_2$ (cf. Figure 2). The previous observation of fluorescence by time-resolved spectrometry[4] for benzanilide in EPA at 77 K we

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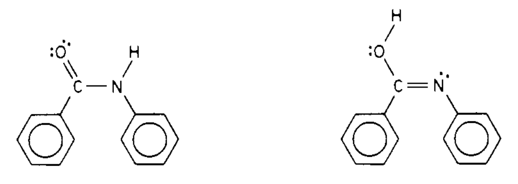


I NORMAL cis (AMIDE) N-PHENYLBENZAMIDE (BENZANILIDE)

II TAUTOMER cis (IMIDOL) N-PHENYLBENZIMIDIC ACID

Figure 1. Amide and imidol forms of benzanilide (*N*-phenylbenzamide).

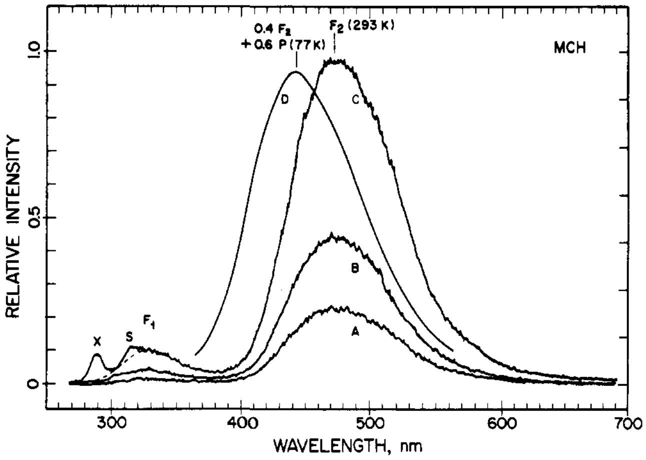


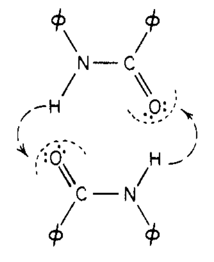
Figure 2. Blue-green fluorescence spectrum F_2 of benzanilide attributed to imidol tautomer produced by double proton transfer in H-bonded dimer, 3.4×10^{-4} M in Na-dried MCH, Ar-degassed. Excitation: (A) 265, (B) 275, (C and D) 285 nm. X, excitation, S, scattering. "Total luminescence" curve D (77 K) is found to represent approximately $0.6P$ and $0.4F_2$ emission.

recognize as mainly F_2, with a weak high-frequency tail representing a very small component of F_1.

The behavior of the F_2 fluorescence of benzanilide can be summarized as follows: (1) The fluorescence intensity at 474 nm increases rapidly with increasing concentration from 10^{-6} to over 10^{-4} M (with provision for constant absorbance). (2) The fluorescence increases in intensity by a large factor as the temperature is lowered. (3) The fluorescence is observed with increasing efficiency as the temperature is lowered toward 77 K in dry degassed MCH and is stable during 6 h of illumination time; in the glass state in MCH, the P/F_2 ratio is approximately 3/2.

The observations eliminate a photochemical product as the source of the blue-green fluorescence. Observations 2 and especially 3 eliminate an *excimer* as a source. We conclude, in exact parallel to the double proton transfer previously studied[5] for 7-azaindole, that a *cis*-benzanilide H-bonded dimer (Figure 3) forms under the conditions described, permitting the double proton transfer leading to the imidol tautomers. Like 7-azaindole, a cyclic ethanol–solute complex can also catalyze the tautomerization, accounting for the EPA results of O'Connell et al.[4]

Figure 4 summarizes the experimental results for the two systems. The S_0, S_1, T_1, etc., molecules of *amide* structure have in common only a topological connectivity map[6] and hence are isomorphous in Peano subspace $\mathcal{P}$; the S_0, S_1, T_1, etc., amide species otherwise have in general different electron density maps, bond lengths, and angles, and could even belong to different point groups. The *imidol* molecules S_0', S_1', T_1', etc., are respectively isomorphous in Peano subspace $\mathcal{P}'$. Thus, the respective spectroscopic diagrams for $\mathcal{P}$ and $\mathcal{P}'$ are unrelated by any fundamental quantum mechanical restriction, and $\Delta E_{S_1'-S_0'}$ for an imidol could be less than $\Delta E_{T_1-S_0}$ for the corresponding amide, as observed. The complete report on this research will develop further the application of changes in molecualr topology in relation to intramolecular proton transfer.



cis-BENZANILIDE
H-BONDED DIMER

Figure 3. H-bonded dimer of *cis*-benzanilide, facilitating double proton transfer in excited ($S_1(\pi,\pi^*)$) state. Dashed arrows refer to *proton* transfer.

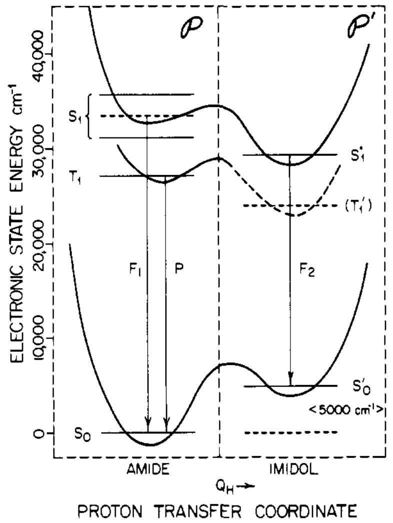


Figure 4. Schematic spectroscopic-correlation for Peano subspace $\mathcal{P}$ isomorphic (amide) species S_0, S_1, and T_1 and Peano subspace $\mathcal{P}'$ (imidol) species S_0', S_1', and T_1' (tautomers) with respect to proton-transfer coordinate. Levels scaled to spectral onsets, S_1 averaging absorption and fluorescence.

Numerous quantum theoretical studies on benzanilide and related molecules have been published,[7-11] but no reliable results seem to be available to indicate $\Delta E_{S_0'-S_0}$, the energy of the imidol ground state above that of amide. We have chosen this to be 5000 cm^{-1} tentatively for benzanilide and its tautomer. A more detailed spectroscopic study will permit an accurate bracketing of this crucial energy magnitude.

Photochemical implications derive immediately from our model. It has been observed that a phenanthridone is a minor photochemical byproduct of benzanilide.[4] In hydrocarbon solutions favoring dimer formation (in the presence of air), the *cis*-imidol form could favor formation of the phenanthridone.

The present observations and interpretation offer a direct means of study of previously inaccessible imidol tautomer of benzanilide and related molecules. We have initiated picosecond dynamics studies of appearance times of $S_{1'}$ and $S_{0'}$ and transient absorption spectroscopy on this system. The complete spectroscopic study of the work summarized here will be published in another place, and the dynamics studies will follow shortly.

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Mechanistic Alternatives in Photocycloaddition of Cyclohexenones to Alkenes[1-3]

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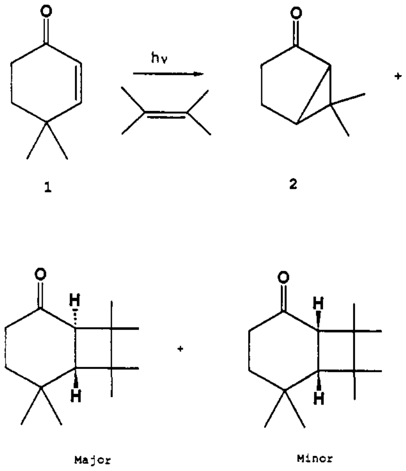
We have previously reported[5] that alkenes linearly quench the photorearrangment of enone **1** to the bicyclic ketone **2** (lumiketone) concomitant with formation of [2 + 2] cycloadducts, implicating a common intermediate on the two reaction pathways.

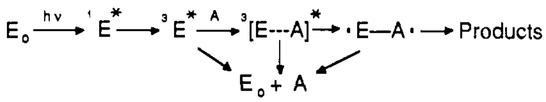


1 2

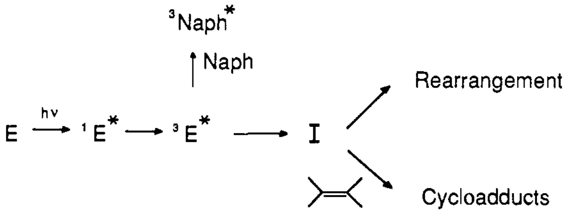
Major Minor

For 2,3-dimethyl-2-butene (TME) in acetonitrile (AN), the quenching slope $k_a\tau$ is 0.48 M^{-1}, where k_a is the rate constant for interaction of TME with an intermediate of lifetime τ derived from enone **1**.[6] Data for several other alkenes is given in Table I. The generally accepted mechanism of enone photoannelation shown in Scheme I, based on the original postulates of Corey[7] as elaborated by de Mayo,[8] involves interaction of an enone (E) triplet excited state with the alkene (A) to give an exciplex, which then proceeds to one or more 1,4-diradicals and thence to products; each of these intermediates could revert back to starting materials. The formation of trans- as well as cis-fused adducts to cyclohexenones[7,9] suggested[5,8c] that the first step involves interaction of twisted enone triplets with the alkenes, consistent with the proposal that such twisted species are intermediates in cyclohexenone photorearrangements.[10] Indeed, naphthalene quenches formation of **2** and the stereoisomeric cycloadducts of **1** with TME in 2-propanol (IPA) to exactly the same extent, confirming that these products arise from a common enone triplet.[11]

Scheme I



Scheme II



Transient absorption observed on laser flash excitation of several conjugated cyclic enones has been ascribed to twisted triplet excited states,[12,13] whose lifetimes vary inversely with the structural rigidity of the C=C bond. The reported triplet lifetime of **1** in AN at room temperature is 25 ± 1 ns;[13] our new measurements[14] give $\tau_T = 27 \pm 2$ ns in AN, 33 ns in IPA, and 24 ns in isooctane, and lifetimes increased only slightly in isooctane when the temperature was lowered to 188 K. If this enone triplet were the species intercepted by TME, k_a would have to be $\sim(2.0 \pm 0.5) \times 10^7$ M^{-1} s^{-1}, in which case reaction of this triplet with high concentrations of TME would be competitive with the unimolecular triplet decay rate of $\sim 4 \times 10^7$ s^{-1}. However, at concentrations up to 3.8 M, TME has no effect on the optical density nor on the rate of decay of the transient from **1** absorbing at 280 nm, consistent with our previous experiments using cyclohexene and 1,1-dimethoxyethylene (DME).[13] Also, in neat cyclopentene, τ_T is 23 ns, indistinguishable from that in isooctane. In addition, TME has no effect on the rate of growth of methylnaphthalene (MN) triplets at 420 nm on excitation of **1** and MN at 337 nm; e.g., $k_q^{MN} = (2.6 \pm 0.6) \times 10^8$ M^{-1} s^{-1} in AN and in AN containing 30% freshly distilled TME (v/v). Extrapolated lifetimes of ^{3}**1*** from plots of k_{growth} vs. [MN] were 26 and 29 ns in AN and in AN containing 30% TME. After reexamination of our earlier data,[13] we conclude that DME also has no effect on triplet energy transfer from ^{3}**1*** to naphthalene (NA).[16] Contrary to our previous conclusions,[13] one enone triplet (or less likely two thermally equilibrated triplets) is sufficient to rationalize all our kinetic data.

Table I illustrates the clear mismatch between values of $k_A\tau$ based on product quenching studies and values of k_q and τ_T determined from flash experiments, using four alkenes in three solvents. Quantum yields for cycloadduct formation given in Table

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