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(27) In one experiment,⁵ 29 was reported inactive.

(28) All melting points are uncorrected. New compounds marked with an asterisk* gave analyses to within ±0.3% of the theoretical, analyses by M–H–W Laboratories, Garden City, Mich. 48135, and Galbraith Laboratories, Knoxville, Tenn. 37921. All compounds were characterized by ir, NMR, and mass spectra but no details are given for results unless worthy of comment. The term "worked up in the usual way" means that a solution of the products in a water immiscible solvent was washed with alkali and/or acid, and with saturated salt solution before filtering the organic solution through a cone of anhydrous MgSO₄.

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Photophysical Properties of β-Amino Ketones. Investigation of Tropinone, N-Methyl-4-piperidone, and 1-Diethylamino-3-butanone

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Abstract: A spectroscopic and photophysical study was carried out on the three β-amino ketones: N-methyl-4-piperidone (2), tropinone (3), and 1-diethylamino-3-butanone (4). Appropriate model compounds representing the amine and ketone chromophores, e.g., N-methylpiperidine and cyclohexanone, respectively, were also examined. Comparisons between the electronic absorption spectra of the amino ketones and the model compounds suggest that 2 and 4 can be considered as bichromophoric (for the lower lying transitions). The absorption spectrum of 3 possesses a moderately strong band at 241 nm which is presumably due to the ground-state coupling between the N n orbital and the carbonyl π orbital. Other correlations are made between absorption and fluorescence and the stereodisposition between the amine and ketone moieties. All three β-amino ketones are characterized by an extremely efficient intramolecular quenching of the amine fluorescence. Thus relative to the quantum yield for the amine fluorescence in N-methylpiperidine, ϕ_f's for the amine emission in 2, 3, and 4 are several orders of magnitude smaller. It is suggested that the mechanism for this quenching arises from energy transfer from the amine to the carbonyl chromophores (which probably proceeds via an exchange-type mechanism). In the case of 3, internal conversion may account, in part, for this quenching. The fluorescence quantum yields of 2 and 3 are typical of model ketones, indicating that the excited-state dynamics of the ketone group are not affected by interaction with the amine function. Carbonyl fluorescence is, however, significantly quenched in 4 implying that this acyclic β-amino ketone can achieve a conformation in which intramolecular quenching of the ketone excited state by the amine group can occur (presumably via an electron (or charge) transfer step). The results of intermolecular quenching studies between alkanones and trialkylamines are discussed in connection with the intramolecular quenching in the β-amino ketones. Sensitized ketone fluorescence was observed as a consequence of the intermolecular quenching of amines by ketones. Photochemical studies indicate that the β-amino ketones (especially 2) are subject to photochemical reduction, probably yielding a highly fluorescent β-amino alcohol as (one of) the photoproduct(s).

The photophysical properties of dialkylaminoalkanones are little known despite the attention given to elucidating the photophysical and photochemical processes of ketones[2] and the intermolecular excited-state interactions between ketones (particularly aryl ketones) and amines.[3] Only recently have the spectroscopic and photophysical properties of trialkylamines been investigated,[4] and a study of the fluorescence of an amino ketone has been reported.[5]

The bicyclic α-amino ketone, 1-azabicyclo[2.2.2]octan-3-one (1), has ben found to exhibit fluorescence characteristic of the ketone group, irrespective of whether excitation was into the amine or ketone transition.[5] Intramolecular energy transfer was invoked to explain this result. The data also indicated the absence of ground-state interaction between the nitrogen lone pair and the carbonyl moiety.

The present work extends the spectroscopic study of 1 into an investigation of a series of β-amino ketones, N-methyl-4-piperidone (2), tropinone (3), and 1-diethylamino-3-butanone
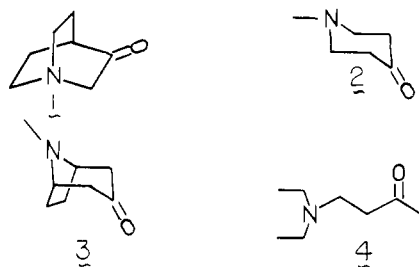
(4), in which the amine and ketone moieties are separated by an additional methylene group as compared with 1. The effect of the separation of the two chromophores by an ethylene linkage, as well as the influence of structure on photophysical properties of the molecule, are of interest.

The possibility that coupling between the amine and carbonyl groups may play a role in the photophysics of β-amino ketones must be considered, as it is well documented that β-
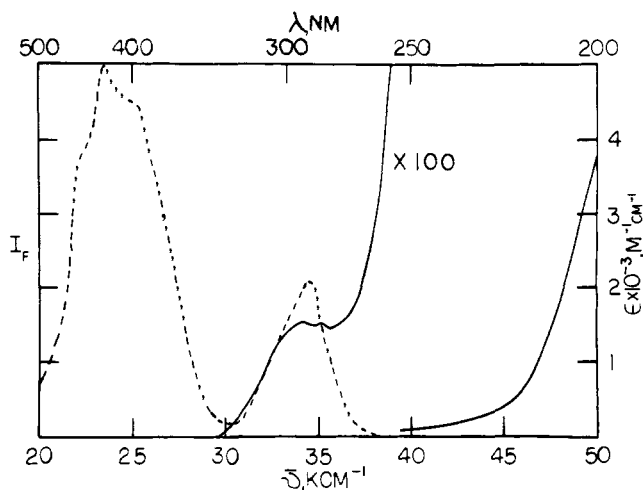
Figure 1. Solution phase absorption and emission spectra of *N*-methyl-4-piperidone (**2**). λ_{exc} = 238 nm.
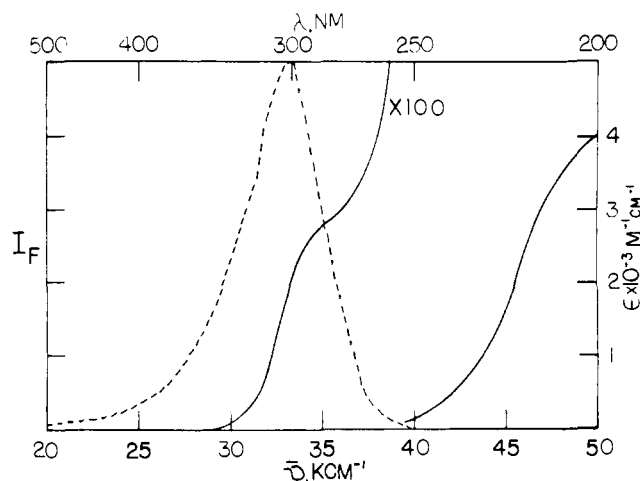

Figure 3. Solution phase absorption and emission spectra of 1-diethyl-amino-3-butanone (**4**). λ_{exc} = 238 nm.

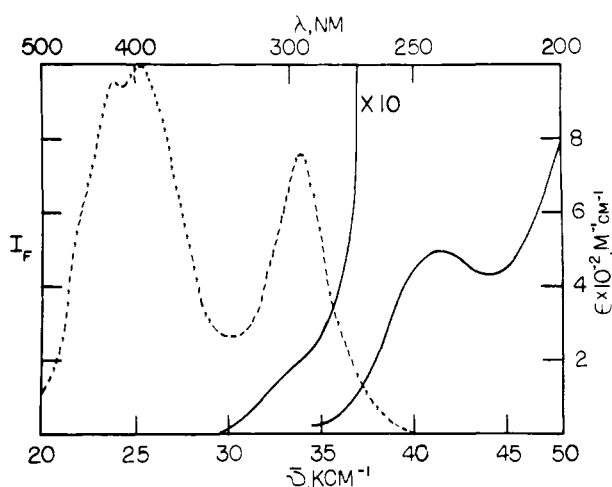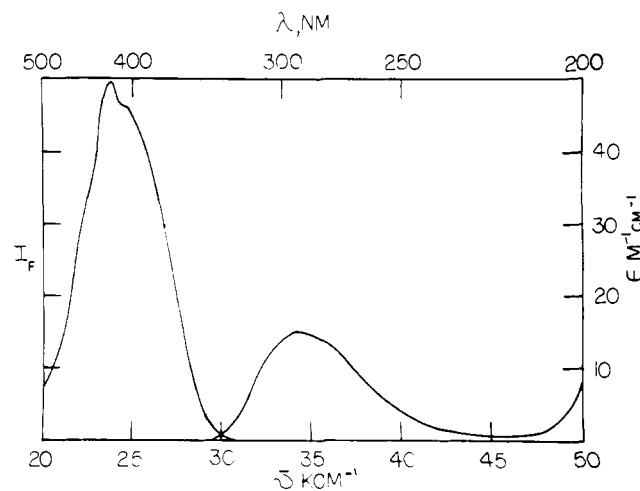**Figure 2.** Solution phase absorption and emission spectra of tropinone (**3**). λ_{exc} = 238 nm.

Figure 4. Solution phase absorption and emission spectra of cyclohexanone. λ_{exc} = 313 nm.

amino ketones of the proper conformation can undergo a thorough σ bond interaction between the nitrogen lone pair and the carbonyl system.[6] The presence of this coupling has been shown via uv spectroscopy,[6a,c-f] circular dichroism,[6c,d] and photoelectron spectroscopy.[7] This type of coupling in the β-amino ketone system is optimal when the nitrogen lone pair, the α,β σ bond, and the p orbitals of the carbonyl group are parallel as represented in **5**, and leads to an optical transition
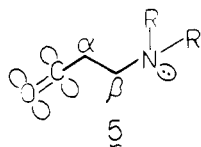
in the 220–260-nm region. This transition has been assigned as the lower energy component of the carbonyl $\pi^* \leftarrow \pi$ transition split as a consequence of coupling with the nitrogen lone pair.[6b,d]

In addition to the three β-amino ketones, this paper also reports the results of a photophysical study of the model compounds cyclohexanone (**6**) and *N*-methylpiperidine (**7**), along with spectroscopic data for a β-amino alcohol, *N*-methyl-4-piperidinol (**8**). The results of studies on the fluorescence self-quenching of **7** and **8**, the fluorescence quenching
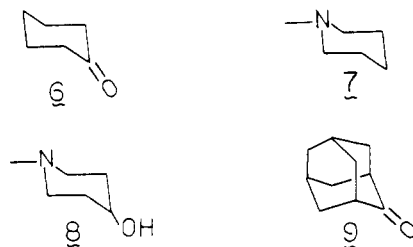
of **7** by 2-adamantanone (**9**), and the fluorescence quenching of **9, 6,** and acetone by **7** are also reported.

Results and Discussions

Spectroscopic Studies. Acyclic **4**, monocyclic **2**, and bicyclic **3** contain the β-amino ketone system in structures of varying rigidity, flexibility, and stereodisposition between the carbonyl and amine chromophores. The results described below indicate that the spectroscopic and photophysical properties of the β-amino ketones reflect the consequences of the different steric arrangements.

The fluorescence and absorption spectra of the three β-amino ketones studied, as well as those of model compounds **6** and **7** are shown in Figures 1–5. From the absorption data contained in Table I, it appears that the absorption spectrum of **2** can be considered the result of adding the two independent
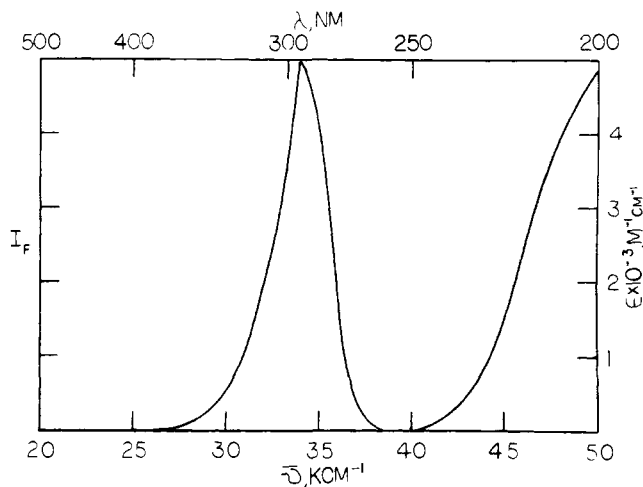
Figure 5. Solution phase absorption and emission spectra of N-methylpiperidine. $\lambda_{exc} = 238$ nm.

Table I. Ultraviolet Absorption Characteristics of β-Amino Ketones and Model Compounds in n-Hexane Solution at 25°

Compd	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ϵ (200 nm)[a]	ϵ (238 nm)[a]	ϵ (290 nm)[a]
2	285	15.1	3710	188	15.1
	293	15.2			
3	241	501	1180	492	22.0[b]
4	199	4090		444	26.4
6	291	15.0	8	2	15.0
7	199	4950		186	
8	196	3870	3750	104	
9	290	16.7		0.88	

[a] These are convenient reference wavelengths and do not correspond to absorption maxima. [b] Shoulder.

chromophores, since the spectrum of **2** is quantitatively similar to those of **6** and **7** in combination. Likewise, the data in Table I indicate that the absorption spectrum of **4** is the sum of appropriate model compounds such as triethylamine[8] and 2-butanone.[9] Thus compound **2** and **4** can be viewed as being comprised of the noninteracting saturated amine and carbonyl chromophores.

This is contrasted, however, by tropinone (**3**), which possesses an electronic transition with λ_{max} at 241 nm[10] which is not characteristic of either the isolated amine or carbonyl chromophore.[5] This σ-coupled transition is considered to be indicative of a group state interaction between the tertiary amine moiety and the carbonyl group.[6a,d] Studies of piperidones,[6a] 1,3-diazaadamantan-6-one,[6e,7a] and 1-azaadamantan-4-one[6f] (**10**) reveal that the conformation responsible for
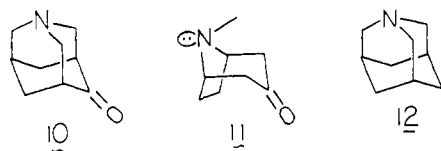
the σ-coupled transition is one in which the amine electron pair is equatorial. Based on this conclusion, it can be inferred that the conformation of **3**, which is responsible for the 241-nm band is **11**, in which the N-methyl substituent is axial and the equatorial nitrogen lone pair is parallel to both the α,β σ bond and to the carbonyl p orbitals.
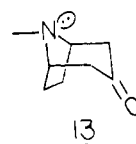
The uv spectrum of **3** is also characterized by a discernible shoulder at 290 nm (see Table I). Similarly, an inflection at 290 nm in addition to a σ-coupled transition at 243 nm (1366 M^{-1} cm^{-1}) is also found in the spectrum of **10**.[6f] As in **3**, the band at 243 nm in **10** is not observed in model compounds, 1-azaadamantane (**12**), (λ_{max} 211 nm (1829 M^- cm^{-1})) and **9** (λ_{max} 290 nm (19 M^{-1} cm^{-1})). The 290-nm shoulder in **10** was attributed to a "local" $\pi^* \leftarrow n$ transition because it has the same energy as the ketone absorption in the model compound **9**.[6f] It was suggested that the energy of the $\pi^* \leftarrow n$ transition need not be affected by coupling with the nitrogen lone pair if the interaction is with the highest occupied π orbital of the carbonyl group.[6f] The same rationalization can be used to explain the identical shoulder in the spectrum of **3** since it appears in the region of the carbonyl $\pi^* \leftarrow n$ transition of structurally similar bicyclic ketones **9** (λ_{max} 290 nm (18 M^{-1} cm^{-1}))[5] and norcamphor (λ_{max} 294 nm (22 M^{-1} cm^{-1})).[5]

An alternative and/or additional explanation for the 290-nm shoulder in the uv spectrum of **3** is that it is an absorption by the tropinone conformer **13** in which the N-methyl group is

equatorial and the nitrogen lone pair axial. It is known that N-alkyl-4-piperidones exist predominantly in a chair form with the N-substituent equatorial, whereas the tropanic system is characterized by a distorted chair conformation with significant populations of both equatorial and axial conformers.[11-14] From the evidence that piperidones with axial nitrogen lone pairs do not possess σ-coupled transitions,[6a] the tropinone conformer **13** is predicted to give rise to absorption characteristics of noninteracting amine and ketone chromophores, analogous to **2**. The 290-nm shoulder, therefore, could be the result of the crowding of the $\pi^* \leftarrow n$ transition of the ketone chromophore (e.g., in **13**) on the tail of the more strongly allowed σ-coupled transition of **11**.[15,16] In addition, the lower extinction coefficient of the σ-coupled transition in **3** (501 M^{-1} cm^{-1}) may be due to the presence of a significant fraction of **13** in the conformation equilibrium of **3**. However, the strength of this σ-coupled transition may be low because the flexible (and probably distorted) piperidone ring of **3** may lessen the coupling efficiency in **3** in comparison to the rigid adamantane framework of **10**.

The results of the fluorescence studies are presented in Table II. The lack of information in the literature regarding the luminescence trialkylamines in solution prompted us to examine the fluorescence characteristics of **7** and **8** in addition to the β-amino ketones. Amines **7** and **8** have fluorescence maxima in the 290–300-nm region and also possess rather high fluorescence quantum yields. These emissive properties are quite characteristic of trialkylamines.[17] The quantum yield and lifetime data contained in Table II represent limiting values at zero concentration because amines **7** and **8** were found to undergo fluorescence self-quenching with rate constants of 4.6 $\times$ 10[9] and 6.3 $\times$ 10[9] M^{-1} s^{-1}, respectively. Unlike the cage amines 1-azabicyclo[2.2.2]octane and 1-azaadamantane, which also self-quench and undergo excimer formation,[18] **7** and **8** exhibit no detectable eximer emission. The latter amines are similar to the acyclic amines triethylamine (k_q in cyclohexane 1.3 $\times$ 10[9] M^{-1} s^{-1}) and diethylmethylamine (k_q in hexane 6.7 $\times$ 10[9] M^{-1} s^{-1}), which also self-quench with less than diffusion-controlled rate constants with excimerization.[19] Steric hindrance may play a role in the contrasting quenching behavior of cage and noncage amines.

The extremely low "amine" fluorescence quantum yields reported for amino ketones **2, 3,** and **4** in Table II require some comment, because the fluorescence quantum yields of tertiary saturated amines (in n-hexane, e.g.) are so large (see ref 17)

Table II. Fluorescence Properties of Several β-Amino Ketones and Model Compounds in n-Hexane Solution at 25°

Compd	Amine fluorescence[a]				Ketone fluorescence[b]			
	λ_{max}, nm	ϕ_f	τ_f, ns[c]	k_r, s^{-1}	λ_{max}, nm	ϕ_f	τ_f, ns[c]	k_r, s^{-1}
2	~300	$\leq 1.6 \times 10^{-4}$			425	1.1×10^{-3}	1.8	6.1×10^5
3	~300	$\leq 5.0 \times 10^{-3}$			384–424[d]	1.0×10^{-3}	1.6	6.2×10^5
4	~300	$\leq 2.7 \times 10^{-2}$			~410	$\leq 1 \times 10^{-5}$		
6					420	1.0×10^{-3}	2.2	4.5×10^5
7	294	0.57	25.0	$2.3 \times 10^{7\,e}$				
8	298	0.51	33.7	$1.5 \times 10^{7\,e}$				

[a] Excitation wavelength is 238 nm. [b] Excitation wavelength is 313 nm. [c] Convoluted values. [d] Broad band centered at ca. 404 nm. [e] These values represent lower limits.[17]

that the presence of a minute amount of an amine in an amino ketone could account for the 300-nm emission reported in Table II. For example, in the case of **2**, an amine could be present at a level of ca. 0.03% to produce an emission with an apparent yield of 1.6×10^{-4} (see also ref 25). This number is reported, therefore, as an upper limit to the intrinsic quantum yield of **2** because, despite the preparative and analytical GLC techniques employed (see Experimental Section), it cannot be absolutely determined that an amine impurity is not present at a level of ca. 0.03%. The 300-nm fluorescence quantum yields of **3** and **4**, being larger, are considered to be more reliable.

Quenching Studies. In the β-amino ketones, the amine fluorescence is vastly extinguished relative to model compounds such as triethylamine and **7**.[17] Thus ϕ_f is smaller by several orders of magnitude, and implies that intramolecular quenching of the amine excited state by the ketone takes place.[20] In contrast to the amine chromophore, the ketone moiety in **2** and **3**, when directly excited, has a "normal" fluorescence quantum yield; i.e., ϕ for these compounds is comparable to model compounds **6** (see Table II), **9**, and norcamphor.[21] The acyclic β-amino ketone **4** is rather unusual in that, unlike **2** and **3**, its carbonyl fluorescence is significantly quenched with ϕ_f smaller by a factor of ca. 100 relative to analogues **2** and **3** (see Table II).

The significant fluorescence quenching of the amine chromophore in the amino ketones can be rationalized by an intramolecular energy transfer process (presumably via an exchange mechanism). This hypothesis is supported by the observation that carbonyl fluorescence is observed not only upon excitation into the $\pi^* \leftarrow$ n transition (313 nm), but also upon irradiation at 238 nm (i.e., by exciting the *amine* chromophore). Moreover, it was determined quantitatively that the intramolecular energy transfer from the 238-nm populated state (excited amine) to the carbonyl $\pi^* \leftarrow$ n state was very efficient (see ref 5).

Further support for the energy transfer quenching mechanism is provided by the fact that ketone **9** *inter*molecularly quenches the fluorescence of amine **7** with very high efficiency ($k_q = 3.2 \times 10^{10}$ M^{-1} cm^{-1} in n-hexane). It is significant that this quenching resulted (at least in part) in the sensitization of ketone **9** (quencher) fluorescence. In this experiment, the excitation wavelength (238 nm) and the quencher (ketone) concentration were such that direct excitation of the ketone was insignificant (see Table I for the relative extinction coefficients).

The phenomenology of the intramolecular quenching of the amine chromophore by the ketone moiety described above could also be thought of as arising from an internal conversion from the amine excited state to the (n, π^*) carbonyl state. However, this view requires that the two chromophores *not* be considered as isolated (or insulated) from each other, but rather as if the respective amine and ketone-type absorptions involve departing and terminating orbitals based on common

atomic centers. The fact that the absorption spectra of amino ketones **1**, **2**, and **4** correlate so well with the respective separated chromophores seems to belie the isochromophore model required in the internal conversion hypothesis.

The magnitude of this rate constant is consistent with the result of studies on singlet excitation transfer requiring collision.[22] The rate constants for the fluorescence quenching of benzene, toluene, and o-xylene by biacetyl in hexane were found to be in the range 3.2–3.5×10^{10} M^{-1} s^{-1}. This value is close to the calculated diffusion-controlled rate constant,[22a] 2×10^{10} M^{-1} s^{-1}, for hexane, and correlates with quenching occurring via collision.

The exchange mechanism must be predominant since the Förster critical distance (R_0) for transfer to biacetyl was calculated to be less than 7 Å, indicating dipole–dipole long-range transfer was not significant. Likewise, R_0 for the amine (donor) 7-ketone (acceptor) **9** pair was calculated to be 2.9 Å, also small primarily because of the low oscillator strength of the ketone $\pi^* \leftarrow$ n transition. The exchange mechanism must also operate in the β-amino ketones since R_0 in those systems should also be on the order of a few angstroms.

The fluorescence lifetimes and quantum yields of the ketone moieties in compounds **2** and **3** are similar to model compounds (such as **9**, **6**, norcamphor), and consequently the radiative rate constants are comparable (see Table II and ref 21). These data imply not only that the ketone $\pi^* \leftarrow$ n transition is unperturbed by the presence of the amine, but also that the dynamics of the ketone n,π^* state are unaffected, and that triplet formation should proceed with usual efficiency.

The intramolecular quenching of the ketone excited state by the amine group in **4** (vide supra) indicates that for this compound, an appropriate conformation for energy removal can be achieved. These results further imply that amino ketones **2** and **3**, for which the ketone fluorescence quantum yields are undiminished, are incapable of reaching a conformation for successful quenching. However, quenching of alkanone fluorescence by trialkylamines appears to be a general phenomenon because intermolecular fluorescence quenching of ketones **9**, **6**, and acetone by amine **7** was observed to take place with moderate efficiency. The quenching rate constants are 5.9×10^8, 1.5×10^9, and 2.0×10^9 M^{-1} s^{-1}, respectively. The values are more than an order of magnitude smaller than the reverse case where the fluorescence of **7** was quenched by **9**. This may reflect the fact that amines cannot quench the ketone excited state by energy transfer. Deactivation, however, could take place via an electron (or charge) transfer mechanism.[23]

Photolysis Studies. It was found that upon photolysis of amino ketones **2**, **3**, and **4** (in degassed n-hexane solution, ca. 1–2×10^{-3} M, at either 238 or 313 nm), a new emission band with λ_{max} in the 294–300-nm region was produced. This contrasts with the behavior of amines **7** and **8** whose fluorescence spectra exhibited no discernible intensity change subsequent to prolonged irradiation at 238 nm. In the case of **2**, which was

examined in most detail, the fluorescence rapidly produced subsequent to photolysis was characterized by λ_{max} of 298 nm and a lifetime of ca. 11 ns. This lifetime represents the fluorescence decay under conditions of appreciable quenching (total quencher concentration is about 10^{-3} M). With the 200-W Xe/Hg lamp employed in this experiment, the 298-nm fluorescence band increased in intensity by a factor of ca. 10 in 60 min with λ_{exc} of 238 nm. When 313 nm was used as the excitation wavelength, the 298-nm emission band increased about 30-fold during the same irradiation time. This difference in the rate of appearance in the 298-nm emission can be attributed to the higher intensity of the 313-nm line vis à vis the 238-nm line of the source.

The uv spectrum of the material produced by the photolysis of **2** revealed an overall increase in optical density and is probably a result of slight turbidity. After prolonged irradiation, the solution became distinctly heterogeneous with the production of a white, powdery precipitate. Thus it was difficult to determine whether or not the photolysis of **2** resulted in a decrease in the optical density of the ketone $\pi^* \leftarrow n$ transition. The photolysis of tropinone (**3**) resulted in the appearance of a fluorescence band at 296 nm, and concomitantly a decrease was observed in the optical density of the σ-coupled transition at 241 nm. The appearance of end absorption was also detected.

The results imply either the carbonyl group is being photoreduced and/or that the amine and carbonyl chromophores are being decoupled (which is a possible consequence of a ring opening process). The fluorescence properties of the photoproduct suggest that it is a tertiary amine which can be generated via photoreduction of the carbonyl group in the β-amino ketone to give the corresponding β-amino alcohol. This process is most likely in light of the known propensity of alkanones (without γ hydrogens) toward photoreduction in hydrocarbon solvents.[24] Upon irradiation of **2**, N-methyl-4-piperidinol (**8**) would be produced along with pinacol and various carbinols and coupling products as shown in eq 1. Compound **8** (see
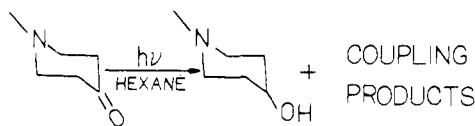

Table II) was shown to match the emissive properties of the photoproduct in being strongly fluorescent with $\tau_f > 10$ ns and a λ_{max} (fluorescence) at 298 nm.[25]

Experimental Section

Materials. The solvent used in these studies was n-hexane, which was obtained from Baker Chemical Co., and purified by a method similar to that described by Zimmerman et al.[26] involving stirring with 10% fuming sulfuric acid, followed by stirring with alkaline KMnO$_4$, and then distillation from KOH. Prior to use, the purified n-hexane was passed through an alumina–silver nitrate column[27] and redistilled from CaH$_2$. The solvent, when degassed, was found to be nonfluorescent within the detection limits of the fluorimeter used. Compounds **9**, norcamphor, and **3** were procured from Aldrich Chemical Co., and twice vacuum sublimed. Toluene and acetone (Baker Chemical Co.) were twice distilled from CaH$_2$. Compounds **2**, **4**, **6**, **7**, and **8** were obtained from either Aldrich or Baker and purified by distillation from CaH$_2$ followed by preparative VPC (either 10% Carbowax 20 M or 10% Apiezon L on 5% KOH coated 60–80 Chromosorb W, 15 ft × ¼ in.).

Spectroscopic Measurements. Uv spectra, as well as the absorbance measurements used in connection with quantum yield determinations, were obtained with a Cary Model 14 spectrophotometer. Fluorescence spectra were obtained using a conventional dc fluorimeter described elsewhere.[28]

Fluorescence Lifetime Measurements. Emission lifetimes were measured using the time-correlated single-photon technique on an apparatus previously described.[29] Data from the multi-channel ana-

lyzer were fed directly or via paper tape into a CDC Cyber 72 computer. Decay curves were displayed using a TSP-212 X-Y plotter (Time Share Peripherals Corp.) interfaced with the computer. Lifetime values were obtained via an interactive program which performed both lamp scatter corrections (where necessary) and convolution calculations.

Quantum Yield Measurements. Toluene ($\phi_f = 0.14$)[5] and norcamphor ($\phi_f = 3.4 \times 10^{-3}$)[5] were used as the quantum yield standards for determining relative fluorescence efficiencies of amine and ketone emission, respectively. Because sample and reference fluorescence occurred in the same spectral region, corrections of the spectra were not necessary. Absorbances at the exciting wavelengths (238 or 313 nm) were kept below 0.3 to avoid inner filter effects and were closely matched. Solutions were degassed by the freeze–pump–thaw technique. The quantum yields for **6** and **7** were corrected for self-quenching.

Quenching Experiments. The fluorescence self-quenching rate constant for amines **7** and **8**, and the fluorescence quenching rate constant of amine **7** by ketone **9** were determined dynamically at room temperature in n-hexane from a plot of τ_f^{-1} vs. [Q], where τ_f is the amine fluorescence lifetime and [Q] is the quencher concentration. The ketone quenching of amine fluorescence was carried out at a constant amine concentration in order to avoid the complications due to amine self-quenching. Amine **7** quenching of the fluorescence of ketones **6**, **9**, and acetone was examined under similar conditions statically, and k_q was calculated from the slopes of plots of I_f^0/I_f vs. [Q]. The unquenched ketone lifetimes were obtained from independent measurements.

Photolysis Experiments. Photolysis of dilute (ca. 10^{-3} M) degassed solutions of **2**, **3**, **4**, **7**, and **8** at various excitation wavelengths was performed using the fluorimeter so that the disappearance and/or growth of fluorescence bands could be conveniently monitored.

Energy Transfer Calculations. Calculations were carried out in order to determine the efficiency of singlet energy transfer via long-range dipole–dipole interaction between the amine donor–acceptor ketone pair, **7** and **9**. R_0, the distance between the donor and acceptor for equal probability of transfer and donor deactivation by all other processes was calculated according to the following expression.[22a]

$$R_0^6 = \frac{8.8 \times 10^{-25} K^2 \phi_D}{n^4} \int_0^\infty F_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$

K^2 is an orientation factor equal to $\frac{2}{3}$ for randomly oriented pairs, ϕ_D is the donor fluorescence quantum yield, n is the refractive index of the solvent and $\int_0^\infty F_D(\nu)\epsilon_A(\nu) \, d\nu/\nu^4$ is the overlap integral between the donor emission spectrum and the acceptor absorption spectrum which was evaluated graphically.

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(17) Unpublished results from this laboratory indicate that ϕ_f's of acyclic trialkylamines such as triethylamine (fluorescence λ_{max} 282 nm) and dimethylethylamine (fluorescence λ_{max} 292 nm) are in the 0.5–0.6 range.
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A Photoisomer of 1,3,6,8-Tetraphenylcyclooctatetraene as a 1:1 Mixture of 1,2,4,7-Tetraphenylcyclooctatetraene and 2,5,7,8-Tetraphenylbicyclo[4.2.0]octatriene in Dynamic Equilibrium. A Structural Enigma

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Abstract: The irradiation of 1,3,6,8-tetraphenylcyclooctatetraene (I) yields a photoisomer. This material, which behaves as a single substance in most tests, was ultimately shown to be a 1:1 mixture of 1,2,4,7-tetraphenylcyclooctatetraene (XV) and 2,5,7,8-tetraphenylbicyclo[4.2.0]octatriene (VIII) in mobile equilibrium at 25 °C.

The irradiation of cyclooctatetraene in the solid,[1] liquid,[2,3] and gas[4] phases yields benzene and acetylene, presumably via the valence isomer bicyclo[4.2.0]octatriene. The photochemical addition of an acetylene to benzene to give a


$$\text{(1)}$$
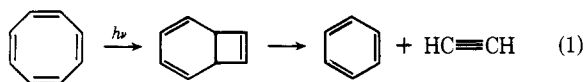
1,2-disubstituted cyclooctatetraene has also been demonstrated, and the bicyclic valence isomer was invoked as a probable intermediate.[5] The bicyclic isomer is also accessible[6] thermally as shown by trapping experiments with dienophiles[7] and by cleavage to give the corresponding acetylene and benzene in the case of a tetracarbethoxycyclooctatetraene.[8] Bicyclo[4.2.0]octatriene has also been synthesized by ground-state reactions;[9] the parent compound is labile, reverting to cyclooctatetraene with a half-life at 0 °C of 14 min.

We report here details of an investigation of the photochemical conversion of 1,3,6,8-tetraphenylcyclooctatetraene (I)[3,10a] into an isomer, A. On the basis of the physical and chemical properties of photoisomer A we conclude that it is a 1:1 mixture of 1,2,4,7-tetraphenylcyclooctatetraene (XV) and 2,5,7,8-tetraphenylbicyclo[4.2.0]octatriene (VIII) in dynamic equilibrium.[10] The *chemical* evidence gathered in the structure proof was ambiguous, and we suspect that this structural problem could not have been solved on the basis of the chemical results alone.

Results

1,3,6,8-Tetraphenylcyclooctatetraene (I) was prepared by treatment of 1,3-diphenyl-2,4-bis(dimethylamino)cyclobutane dimethiodide with a strong base.[12] Yields of about 30% of I were achieved accompanied by 1,3,5,7-tetraphenylcyclooctatetraene (II, 39%) and smaller amounts of other products.[1,13]

Photochemistry of 1,3,6,8-Tetraphenylcyclooctatetraene (I). The irradiation of compound I under a variety of conditions yielded a photoisomer, A (eq 2). Hexane solutions of I were

$$C_6H_5C{\equiv}CC_6H_5 + C_6H_5{-}\langle{\bigcirc}\rangle{-}C_6H_5 \qquad \text{(2)}$$
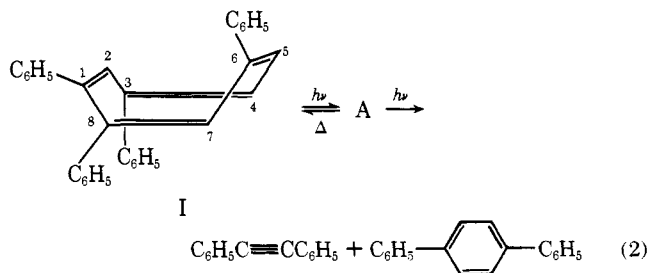
irradiated with 40-W General Electric "Cool White" fluorescent lights, 275-W General Electric sunlamps, and 450-W Hanovia mercury lamps. Whether solutions were degassed and sealed under vacuum or irradiated while open to the atmosphere appeared to make no significant difference. In all cases, the concentration of I decreased during irradiation while the concentration of A increased first (to a maximum of about 58%