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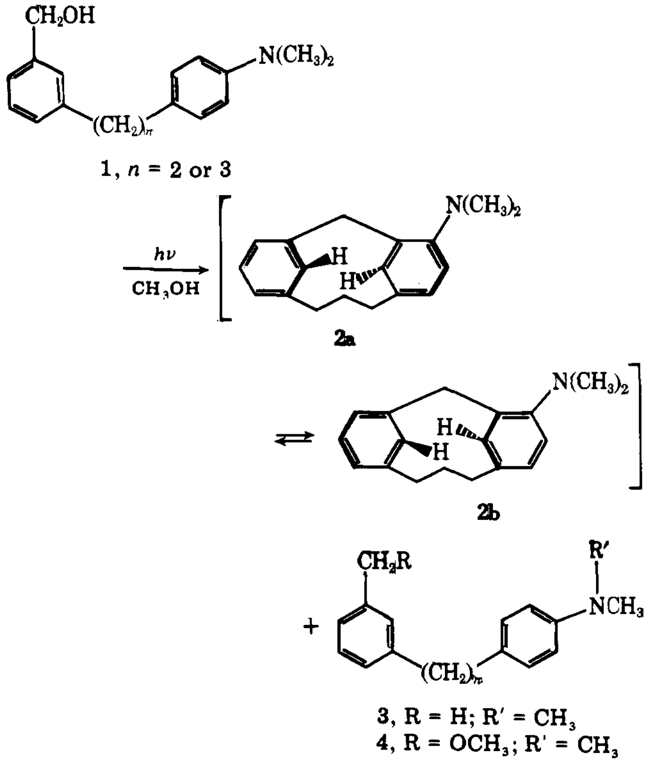
Photochemical Preparation of a [3.1]Metacyclophane and [3.2]Metaparacyclophane through Internal Charge-Transfer Sensitization

Sir:

A recent publication by Atzmüller and Vögtle[1] on the low yield preparation of [4.1]metacyclophane and their unsuccessful attempt to prepare the lower [3.1] homologue prompts us to communicate the photochemical synthesis and spectral properties of a novel [3.1]metacyclophane and 1-aza[3.2]-metaparacyclophane.

The benzyl alcohol **1** ($n = 3$) was prepared by $NaOC_2H_5$ catalyzed condensation of ethyl *m*-acetylbenzoate with *p*-dimethylaminobenzaldehyde, followed by sequential catalytic (Pd/C) and $LiAlH_4$ reduction of the resulting chalcone (40% overall yield).[2] Irradiation of a deoxygenated methanol solution of **1** ($n = 3$) using Pyrex-filtered light (Rayonet reactor, 300 nm) afforded, after TLC on silica (30% ether-petroleum ether), 34% [3.1]metacyclophane[2] (**2**) and 37% recovered **1**. In addition there were isolated compounds **3–5** ($n = 3$) in 2, 9, and 4% yield, respectively, which were shown by their NMR spectra to have the *N*-methyl and/or hydroxyl groups of **1** replaced.



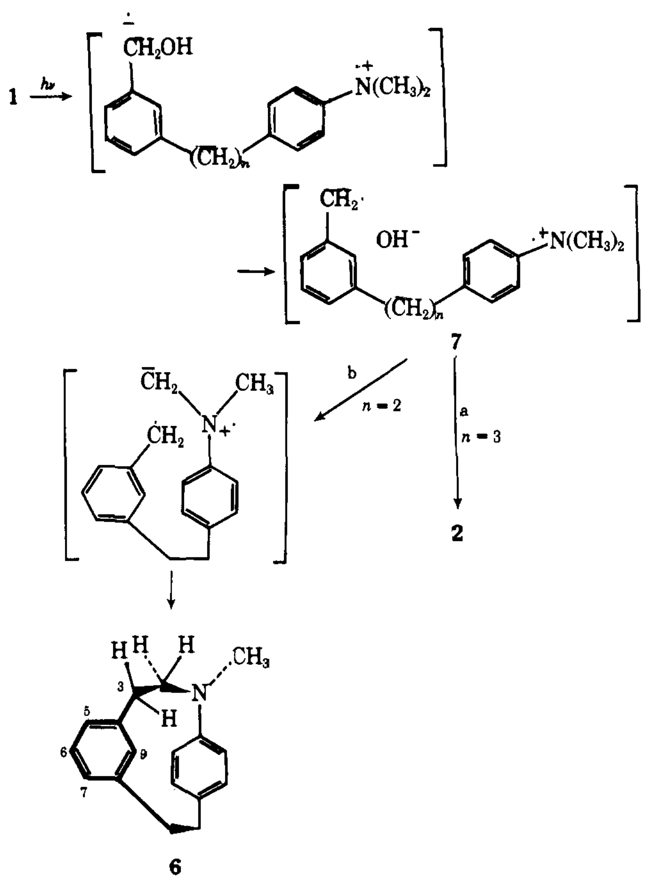
1, $n = 2$ or 3

2a

2b

3, R = H; R' = CH_3
4, R = OCH_3; R' = CH_3
5, R = OCH_3; R' = H

Scheme I



The ultraviolet absorption of compound **2** was shifted to longer wavelength [λ_{max}^{MeOH} 323 nm (ϵ 1250)] than the starting benzyl alcohol [λ_{max}^{MeOH} 302 nm (ϵ 1650)] and displayed a shoulder in place of the maximum of the latter compound at 254 nm in accord with the presence of a distorted benzene ring in the molecule.[3] The structure **2** was further supported by the NMR spectrum ($CDCl_3$) which showed at −30 °C an AB quartet (CH_2) at δ 3.58 and 4.20 (J = 17 Hz) and highly shielded aromatic singlets at δ 5.44 (1 H) and 5.91 (1 H). In addition, complex multiplets were observed at δ 1.7 (2 H) and 2.5 (4 H) for the propylene hydrogens and at δ 6.8 (5 H) for the remaining aromatic protons. The two methyl groups appeared as a singlet at δ 2.80. The AB quartet coalesced to a broad singlet at 68 °C and total band shape analysis[4] using a modified QUABEX[5] computer program yielded rate constants for the expected conformational interconversion **2a** ⇄ **2b** which increased from 1.8 s^{-1} at 13 °C to 3300 s^{-1} at 109 °C. Using the Eyring equation[6] and assuming a unit transmission coefficient,[5] the activation parameters $\Delta H^{\ddagger} = 16.3$ kcal/mol and $\Delta S^{\ddagger} = -0.21$ cal/deg were obtained.

For purpose of comparison with other values, the rate of exchange was determined at the coalescence temperature from the relationship[7] $k_c = \pi[(\Delta\nu^2 + 6J^2)/2]^{1/2}$ and gave $\Delta F^{\ddagger}$ = 16.7 kcal/mol. This energy is much lower than that of the rigid [2.2]metacyclophane (>27 kcal/mol)[8,9] and is similar to the homologous [3.2]metacyclophanes (15.8–19.1 kcal/mol).[10] The reported value[1] for the more flexible [4.1]metacyclophane of $\Delta F^{\ddagger}$ = 19.6 kcal/mol at 115–120 °C is based on a questionable NMR analysis and appears from the present data to be too high.

Attempts were made to prepare a highly strained [2.1]-metacyclophane by irradiation of alcohol **1** ($n = 2$). This compound was prepared in 81% yield by Wittig condensation of *m*-carbomethoxybenzyltriphenylphosphonium bromide and *p*-dimethylaminobenzaldehyde followed by $LiAlH_4$ reduction (Et_2O) and catalytic (Pd/C) hydrogenation. Irradiation of **1** ($n = 2$) followed by TLC on silica yielded none of the desired [2.1]metacyclophane. Instead, the unexpected *N*-methyl-1-

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aza[3.2]metaparacyclophane **6** was isolated (3%) along with 32% recovered **1** ($n = 2$) and compounds **3-5** ($n = 2$) in 3, 57, and 3.5% yield, respectively.[2] The structure of **6** was supported by the replacement of the characteristic ultraviolet maximum of **1** ($n = 2$) at 302 nm with a broad featureless absorption extending to a maximum at 254 nm (ϵ 5250) in methanol. The pK_a, determined spectroscopically in methanol-water and extrapolated to pure water, was 6.92, significantly higher than 5.06 obtained for *N,N*-dimethylaniline. Both phenomena are in good accord with the expected effect of twisting the amino group out of the plane of the aromatic ring.

The 200-MHz NMR spectrum ($CDCl_3$) of **6** at −60 °C displayed an *N*-methyl peak at δ 2.78 (3 H). The C-9 aromatic proton signal was a triplet at δ 5.33 and the remaining three protons of the meta-substituted ring were centered at δ 6.76 and 7.1 ($J_{6,7} = 7.95$, $J_{5,6} = 6.92$, $J_{5,7} = 1.74$, $J_{7,9} = 1.25$, and $J_{5,9} = 1.78$ Hz). The hydrogens of the para-substituted ring appeared as AB quartets at δ 5.73 and 6.18 ($J = 8$ Hz) and at δ 6.94 and 7.10 ($J = 8$ Hz). At 15 °C the δ 6.18 and 6.94 bands coalesced and at 60 °C were replaced by a broad signal at δ 6.53. The δ 5.73 and 7.10 signals merged into a broad shoulder at δ 6.36 at this temperature. Using the expression[7] $k_c = \pi\Delta\nu\sqrt{2}$, these observations lead to an approximate $\Delta F^{\ddagger}$ for interconversion of 13.5 kcal/mol.

The C-2 and C-3 methylenes protons of **6** at 25 °C appeared as multiplets at δ 3.5 and 2.3. In **6**, C(3)-d_2, which was prepared from the corresponding α-deuterated alcohol **1** ($n = 2$), the C-2 hydrogens appeared at −40 °C as an AB quartet at δ 3.39 and 3.82 ($J = 15$ Hz) which coalesced at 10 °C, $\Delta F^{\ddagger} = 14.0$ kcal/mol. Exchange of the C(2) protons can only be accommodated by flipping of the meta-substituted ring with consequent transformation of the chiral structure **6** to its enantiomer. Although this transformation also results in exchange of the protons of the para-substituted ring, independent rotation of the latter ring could produce the same effect. The 0.5-kcal/mol lower activation energy for exchange of the protons of the para-substituted ring lies close to the sensitivity of the method but suggests that the latter ring may rotate independently and at a similar rate to enantiomeric interconversion.

In analogy to the photochemical condensation of benzyl alcohol with *N,N*-dimethylaniline,[11] the [3.1]metacyclophane **2** is probably formed by cyclization of **7** either before or after internal electron transfer (Scheme I, path a). The formation of the [3.2]metaparacyclophane **6** may occur through proton abstraction by OH^- within the ion pair **7** (Scheme I, path b). Successful competition of this pathway over cyclization to a highly strained [2.1]metacyclophane would not be surprising. Abstraction of a proton from the *N*-methyl in **7** has precedent in the abstraction of protons from amine radical cations by ketone radical anions.[12] While abstraction by anions lacking an unpaired electron does not appear to have been reported, OH^- is a stronger base than the ketyl radical anion[13] and proton transfer to it is energetically reasonable. In agreement with this mechanism the ratio of methyl ether **4** ($n = 2$) to cyclophane **6** increased from ~14 to >62 when the benzyl chloride corresponding to **1** ($n = 2$) was irradiated in place of **1** ($n = 2$) so as to form chloride ion instead of the more basic OH^-. For these experiments short irradiation times were used to avoid secondary photolysis of **4** ($n = 2$) since the latter compound can be converted photochemically into **6** in up to 12% yield (31% based on recovered starting material).

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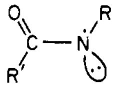
The Structure of Amidyl Radicals. An Investigation by Variable-Temperature Electron Paramagnetic Resonance Spectroscopy[1]

Sir:

There have been many attempts to determine whether amidyl radicals (*N*-alkylcarboxamidyls, $R'CO\dot{N}R$) have a π or σ electronic ground state. Both the π (**1**) and σ_N (**2**) states have been suggested to participate in chemical reactions.[2] The EPR data[3-5]—which is limited in the extreme[6]—has been tentatively interpreted in terms of a π configuration.[3,7] However, bent σ_N (**2**) and linear σ_N (**3**) configurations cannot be excluded.[13]



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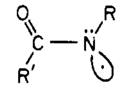

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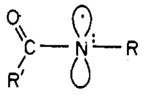

3

We have examined the EPR spectra of a variety of amidyls over the widest range of temperatures possible in each case. The amidyls were generated by photolysis of the *N*-chloramides in cyclopropane (cyclopropane–ethylene for the lowest temperatures), which is the procedure pioneered by Danen and Gellert.[3] In this communication we concentrate on just four amidyls and on the magnitude and temperature dependence of their a^{H_β} parameters (the H hyperfine splittings (hfs) of the $NCH_\beta R''R'''$ groups).[14] The experimental results, which are shown in Figure 1, can be interpreted *only* in terms of the π configuration, **1**. Both the bent (**2**) and linear (**3**) σ_N configurations can finally be excluded.

The generally accepted relationship between a^{H_β} and θ, the dihedral angle between the C–H_β bond, and the axis of the semioccupied orbital is[15]

$$a^{H_\beta} = A + B\cos^2\theta$$

where A and B are constants, and A can usually be neglected.[16] In $EtCO\dot{N}CH_3$ the average value of θ is 45° at all temperatures and, since $a^{H_\beta} = 29.5$ G, it follows that $B \approx 59$ G. We have found for $EtCO\dot{N}CH_2Me$, and related radicals,[17] that a^{H_β} is always >29.5 G and that there is a very large variation in a^{H_β} with temperature.[18] The value of a^{H_β} *decreases* with *increasing* temperature and approaches the temperature invariant value found for $EtCO\dot{N}CH_3$. At the lowest temperature attained (109 K), $EtCO\dot{N}CH_2Me$ has $a^{H_\beta} = 43.3$ G and hence the *average* value of the dihedral angle, $\bar{\theta}$, is ~30°, while at higher temperatures $\bar{\theta}$ tends toward the "free rotation" value of 45°. This behavior is analogous to that found for alkyl radicals of the type $R_1R_2\dot{C}CH_2R_3$ in which $\bar{\theta}$ also becomes smaller as the temperature is reduced.[15]

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