BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 709—710 (1975)

# The Effect of Partial Deuteration on the Phosphorescence Lifetime of *N*,*N*,*N'*,*N'*-Tetramethyl-*p*-phenylenediamine

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(Received June 24, 1974)

**Synopsis.** A position-dependent deuterium effect on the phosphorescence lifetime of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine was found. Aromatic ring protons and methyl protons were shown to contribute to the radiationless transition independently and differently. Important terms in the decay constant are briefly discussed.

Phosphorescence lifetimes have been measured for *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD) and its deuterium derivatives; (I) $(CH_3)_2N\text{-}C_6H_4\text{-}N(CH_3)_2$, (II) $(CH_3)_2N\text{-}C_6H_2D_2\text{-}N(CH_3)_2$, (III) $(CH_3)_2N\text{-}C_6D_4\text{-}N(CH_3)_2$ (91%), (IV) $(CD_3)_2N\text{-}C_6H_4\text{-}N(CD_3)_2$ (94%), and (V) $(CD_3)_2N\text{-}C_6D_4\text{-}N(CD_3)_2$ (85%).
II—V were prepared by ammonolysis of *p*-dibromobenzenes in an autoclave under a nitrogen pressure of 25 kbar followed by methylation with dimethyl sulfate in $H_2O$ or $D_2O$.[1,2] Values in parentheses are the isotopic purities measured by low-voltage mass spectroscopy. II was a mixture of compounds in which deuterium was distributed statistically on the aromatic ring and NMR spectra showed its deuterium content to be ~50%. All samples were dissolved in 3-methylpentane(3MP) or in EPA, degassed with 6—7 freeze-thaw cycles. Phosphorescence lifetimes were measured at 77 K by a standard technique and the triplet decay was displayed on a Riken Denshi High Speed SP-J-5V recorder. The observed decays were exponential over 3—4 lifetimes. The results are listed in Table 1. $k_{\mathrm{II}}$ contains a considerable error, as II was a mixture of compounds with different rate constants. It was not discarded because the main part of $k_{\mathrm{II}}$ seems to come from the doubly substituted compound.

Following Watts and Strickler,[3] the triplet decay constant was expressed as

$$k = \tau^{-1} = k_{\mathrm{d}} + N_{\mathrm{me}}k_{\mathrm{me}} + N_{\mathrm{ar}}k_{\mathrm{ar}}\,,$$

where $k_{\mathrm{d}}$ is the decay constant in the perdeuterated TMPD (V), $N_{\mathrm{me}}$ and $N_{\mathrm{ar}}$ are the numbers of methyl and aromatic ring protons, and $k_{\mathrm{me}}$ and $k_{\mathrm{ar}}$ represent changes in the radiationless rate constants when a proton is replaced by a deuteron at the methyl or aromatic ring position, respectively. Our data fitted well to this equation with the least squares values of $k_{\mathrm{d}}=0.185$, $k_{\mathrm{me}}=0.0046$, and $k_{\mathrm{ar}}=0.030\ \mathrm{s}^{-1}$ in 3MP, and $k_{\mathrm{d}}=0.168$, $k_{\mathrm{me}}=0.0038$, and $k_{\mathrm{ar}}=0.029\ \mathrm{s}^{-1}$ in EPA. The coincidence is striking as can be seen from the last colume of Table 1. It shows that not only protons at different positions of an aromatic ring, but protons of different groups conform well to Watts' equation. An aromatic ring substitution was 6—8 times more effective in decreasing the decay rate than a methyl substitution. In contrast to toluene in which the methyl protons have a negligible effect,[4] those of TMPD showed a small but difinite effect. Generally lifetimes were longer in EPA than in 3MP.

Table 1. Triplet decay times and rate constants of partially deuterated TMPD

| Solvent | Compound | $\tau$ (s) | $k_{\mathrm{obs.}}$ ($\mathrm{s}^{-1}$) | $k_{\mathrm{calc.}}$ ($\mathrm{s}^{-1}$) | $\Delta k$ (%) |
|---|---|---|---|---|---|
| 3MP | I | 2.7 | 0.37 | 0.36 | −2.7 |
| | II | 3.4 | 0.29 | 0.30 | +3.4 |
| | III | 4.2 | 0.24 | 0.24 | 0 |
| | IV | 3.3 | 0.30 | 0.31 | +3.3 |
| | V | 5.3 | 0.19 | 0.19 | 0 |
| EPA | I | 2.9 | 0.34 | 0.33 | −2.9 |
| | II | 4.0 | 0.25 | 0.27 | +8.0 |
| | III | 4.5 | 0.22 | 0.21 | −4.5 |
| | IV | 3.6 | 0.28 | 0.28 | 0 |
| | V | 5.9 | 0.17 | 0.17 | 0 |

The radiationless rate constant is represented by

$$\begin{aligned} k = \frac{2\pi}{\hbar}\rho \sum_{l} \Bigg| & \langle f|H_{\mathrm{so}}|i\rangle \prod_{m} \langle \chi^{\mathrm{f}}_{m,l}|\chi^{\mathrm{i}}_{m}\rangle \\ & - \sum_{n} \frac{\hbar^2}{\mu_n}\left[\sum_{j} \frac{\langle f|H_{\mathrm{so}}|j\rangle \left\langle j\left|\frac{\partial}{\partial Q_n}\right|i\right\rangle}{E_j-E_f} \right. \\ & \left. + \sum_{k} \frac{\left\langle f\left|\frac{\partial}{\partial Q_n}\right|k\right\rangle \langle k|H_{\mathrm{so}}|i\rangle}{E_k-E_i}\right] \\ & \times \left\langle \chi^{\mathrm{f}}_{n,l}\left|\frac{\partial}{\partial Q_n}\right|\chi^{\mathrm{i}}_{n}\right\rangle \prod_{m\neq n} \langle \chi^{\mathrm{f}}_{m,l}|\chi^{\mathrm{i}}_{m}\rangle \Bigg|^2, \end{aligned}$$

where $i$ and $f$ denote initial and final pure spin electronic states and $j$ and $k$ are virtual pure spin states. $\chi^{\mathrm{i}}_{s}$ and $\chi^{\mathrm{f}}_{s,l}$ are the vibrational wave-functions coresponding to the normal coordinate $Q_s$ and belonging to the mixed spin initial and final Born-Oppenheimer states, which we were to observe. Here, $n$ refers to the promoting mode and $m$ to the accepting mode. Suffix $l$ runs over the final Born-Oppenheimer manifold $\Psi^{\mathrm{f}}_{l}$, isoenergetic with each other and with the initial state, and belonging to a single mixed spin electronic state.

Assuming that a single accepting mode is excited in each of $\Psi^{\mathrm{f}}_{l}$ and ignoring the contribution of $\chi^{\mathrm{f}}_{n,l}$ to the energy of $\Psi^{\mathrm{f}}_{l}$, the sum over $l$ can be replaced by the sum over $m$, so that the leading term in $k$ becomes

$$k = [\langle S\rangle + \sum_{n}\langle P_n\rangle] \sum_{m}\langle A_m\rangle$$

with

$$\langle S\rangle = \frac{2\pi}{\hbar}\rho\,|\langle f|H_{\mathrm{so}}|i\rangle|^2$$

$$\langle P_n\rangle = \frac{\pi\hbar^3}{\mu_n^2}\rho\left|\left[\sum_j \frac{\langle f|H_{\mathrm{so}}|j\rangle\left\langle j\left|\frac{\partial}{\partial Q_n}\right|i\right\rangle}{E_j-E_f} + \sum_k \frac{\left\langle f\left|\frac{\partial}{\partial Q_n}\right|k\right\rangle\langle k|H_{\mathrm{so}}|i\rangle}{E_k-E_i}\right]\left\langle \chi_n^{\mathrm{f}}\left|\frac{\partial}{\partial Q_n}\right|\chi_n^{\mathrm{i}}\right\rangle\right|^2$$

and

$$\langle A_m\rangle = |\langle \chi_m^{\mathrm{f}}|\chi_m^{\mathrm{i}}\rangle|^2$$

where $\chi_{n,l}^{\mathrm{f}}$ has been replaced by $\chi_n^{\mathrm{f}}$ in accordance with the selection rule. In TMPD, the first term, $\langle S\rangle$, vanishes by symmetry.[5] For the promoting mode, $n$, Burland and Robinson[6] claimed that non-totally symmetric in-plane skeletal modes ($b_{2u}$ in benzene) cause radiationless transition by contributing to the $\pi$-$\pi$ Herzberg-Teller matrix elements, whereas Henry and Siebrand[7] stressed the importance of C–H out-of-plane modes which are responsible for $\sigma$-$\pi$ vibronic terms due to breakdown of the Born-Oppenheimer approximation. The latter mechanism was used to account for the position dependent deuterium effect in benzene, naphthalene[7] and anthracene.[8] However, the relative importance of these two mechanisms has not yet been established. From our data we shall make a rough estimate of the relative contribution of two mechanisms. For simplicity, we take only three terms for the promoting modes; skeletal modes, ring C–H out-of-plane modes and ring C–D out-of-plane modes. Notations ⟨CC⟩, ⟨CH⟩ and ⟨CD⟩ stand for the terms $\langle P_n\rangle$ containing these modes. For the accepting mode $m$, there seems to be little doubt that the C–H stretching modes are most important: we retain only these modes in the present approximation. As the C–H bonds of the ring and those of the methyl group contribute different amounts, we denote their Franck-Condon integrals with ⟨R⟩ and ⟨M⟩, respectively. There are as many terms as there are normal modes, and these symbols represent sums of like terms. The rate of a radiationless transition is expressed by a sum of product terms; ⟨CC⟩⟨R⟩, ⟨CH⟩⟨R⟩, ⟨CD⟩⟨R⟩, ⟨CC⟩⟨M⟩, ⟨CH⟩⟨M⟩, and ⟨CD⟩⟨M⟩. For example $k_{\mathrm{I}}=k_0+\langle \mathrm{CC}\rangle\langle \mathrm{R}\rangle+\langle \mathrm{CH}\rangle\langle \mathrm{R}\rangle+\langle \mathrm{CC}\rangle\langle \mathrm{M}\rangle+\langle \mathrm{CH}\rangle\langle \mathrm{M}\rangle$, $k_{\mathrm{III}}=k_0+\langle \mathrm{CC}\rangle\langle \mathrm{M}\rangle+\langle \mathrm{CD}\rangle\langle \mathrm{M}\rangle$ and $k_{\mathrm{IV}}=k_0+\langle \mathrm{CC}\rangle\langle \mathrm{R}\rangle+\langle \mathrm{CH}\rangle\langle \mathrm{R}\rangle$, where $k_0$ represents the radiative rate constant. Then $k_{\mathrm{I}}-k_{\mathrm{IV}}=0.070$ (3MP) corresponds to $\{\langle \mathrm{CC}\rangle+\langle \mathrm{CH}\rangle\}\langle \mathrm{M}\rangle$ and $k_{\mathrm{III}}-k_{\mathrm{V}}=0.050$ to $\{\langle \mathrm{CC}\rangle+\langle \mathrm{CD}\rangle\}\langle \mathrm{M}\rangle$. Taking the ratio of these two expressions, we obtain

$$\frac{\langle \mathrm{CC}\rangle+\langle \mathrm{CD}\rangle}{\langle \mathrm{CC}\rangle+\langle \mathrm{CH}\rangle} = 0.71\,,$$

According to Siebrand,[7] ⟨CD⟩/⟨CH⟩ is roughly equal to $\omega_{\mathrm{D}}\mu_{\mathrm{H}}/\omega_{\mathrm{H}}\mu_{\mathrm{D}}$, where $\omega_{\mathrm{H}}$ and $\omega_{\mathrm{D}}$ are the frequencies and $\mu_{\mathrm{H}}$ and $\mu_{\mathrm{D}}$ are the reduced masses of the corresponding normal modes. Our measurement shows that

$$\frac{\omega_{\mathrm{D}}\mu_{\mathrm{H}}}{\omega_{\mathrm{H}}\mu_{\mathrm{D}}} = \frac{720}{812}\times\frac{7}{13} = 0.48\,,$$

which leads to

$$\frac{\langle \mathrm{CH}\rangle}{\langle \mathrm{CC}\rangle} = 1.3 \quad (\mathrm{3MP})\ .$$

A similar calculation gives 0.5 for EPA. The difference may be attributed to the rough approximation employed and to errors in the measured values. We can only infer that neither mechanism can be ignored. To account for the large difference in $k_{\mathrm{ar}}$ and $k_{\mathrm{me}}$, we compare $k_{\mathrm{I}}-k_{\mathrm{IV}}$ with $k_{\mathrm{IV}}-k_{\mathrm{V}}$,

$$\frac{k_{\mathrm{I}}-k_{\mathrm{IV}}}{k_{\mathrm{IV}}-k_{\mathrm{V}}} = \frac{\langle \mathrm{CC}\rangle\langle \mathrm{M}\rangle+\langle \mathrm{CH}\rangle\langle \mathrm{M}\rangle}{\langle \mathrm{CC}\rangle\langle \mathrm{R}\rangle+\langle \mathrm{CH}\rangle\langle \mathrm{R}\rangle} = \frac{\langle \mathrm{M}\rangle}{\langle \mathrm{R}\rangle}\,.$$

This ratio is 0.6 in 3MP and 0.5 in EPA. Note that there are four terms in ⟨R⟩ and twelve terms in ⟨M⟩. The large difference between $k_{\mathrm{ar}}$ and $k_{\mathrm{me}}$ may therefore be attributed to the difference in Franck-Condon factors. As the ring protons are attached directly to the carbon atoms which carry $\pi$-electrons, it is quite natural that the electronic excitation causes a change in the ring C–H stretching normal modes to give a large $k_{\mathrm{ar}}$ value. The absence of contributions to the radiationless rate constant from alkyl groups in alkylbenzenes can be understood as they are separated from the $\pi$-electron center. In TMPD, however, the charge density at the nitrogen atom, which carries $\pi$-electrons, changes considerably when the molecule is excited, and this may have an inductive effect on methyl C–H bonds giving rise to a moderate deuterium effect.

## References

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4) D. M. Haaland and G. C. Nieman, *ibid.*, **59**, 1013 (1973).

5) If we assume $D_{2h}$ pseudosymmetry for the molecule, the lowest triplet is $B_{3u}$. The presence of methyl groups slightly offsets the $D_{2h}$ symmetry, but affects little on the selection rule. The detailed calculation will be presented elsewhere.

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