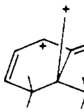
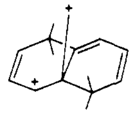
the transmission of conjugation between two substituents via a cyclopropane bond is known to be very small.[21] The greater stability of **3** compared with **4** also follows from a comparison of the extreme resonance structures **10** and **11** in which the



10



11

C(6)-C(11) bond is broken. The stabilizing contribution of **11** to **4** will be far less than that of **10** to **3** in view of the stronger inductive repulsion between the two charges with **11** (via two σ bonds) than **10** (via three σ bonds), the direct field effect in both structures being the same.

Carbodications were reported very recently, but only as transient intermediates, e.g., the Wheland intermediates for the H-D exchange of an aromatic cyclopropenium ion[22] and monoprotonated 3-hydroxyphenalenone[23] or as species containing conjugative stabilizing electron-donating oxygen substituents, like the protonated 2,2′,2″,6,6′,6″-hexamethoxytrityl cation[23] and diprotonated 3-hydroxyphenalenone.[24] The present dication **3** is the first reported stable dication which is devoid of this type of electron-donating heteroatom substituents.

In conclusion evidence is presented that the 1,1-diallylcyclopropane moiety of the dication **3** has the allylcyclopropane elements in fixed geometries comparable with that calculated for conformation **6** of the cyclopropylcarbinyl monocation. Further and more detailed work on the protonation of annulenes is currently in progress.

Acknowledgment. We thank Professor E. Vogel (Cologne) for stimulating our present investigations, Professor J. W. Verhoeven for stimulating discussions, and Mr. C. Kruk for assistence in obtaining the NMR spectra.

References and Notes

(1) Part 4: Van de Griendt, F.; Cerfontain, H. *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.
(2) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964,** *76*, 145. (b) Vogel, E.; Klug, W.; Breur, A. *Org. Synth.* **1974,** *54*, 11.
(3) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1978,** *100*, 8244.
(4) See the discussion in ref 3.
(5) (a) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979,** *101*, 3618. (b) Van de Griendt, F.; Cerfontain, H. *Tetrahedron* **1979,** *35*, 2563; (c) *Ibid.*, **1980,** *36*, 317.
(6) Warner, P.; Winstein, S. *J. Am. Chem. Soc.* **1969,** *91*, 7785.
(7) Careful protonation at very low temperatures initially afforded the ion solution of **2** (orange-red)[8] which upon temperature increase gradually darkened and yielded the ion solution of **3** as was established by NMR spectroscopy.
(8) The ^{13}C NMR data of **2** will be reported in the full paper.
(9) At temperatures >-60 °C an additional monocation is observed, owing to a rearrangement of **2** (see also ref 6). This rearrangement will be the subject of a forthcoming report.
(10) These four ^{1}H NMR absorptions are also in accordance with the C_2 symmetry of **4,** the structure of which would compare with the structures of the dications of hexa- and octamethylnaphthalene.[11] However, for that ion the ^{13}C NMR spectrum should display six instead of the observed seven absorptions.
(11) Bodoev, N. V.; Mamatyuk, V. I.; Krysin, A. P.; Koptyug, V. A. *J. Org. Chem. USSR* **1978,** *14*, 1789.
(12) Günther, H.; Schmickler, H.; Bremser, W.; Straube, F. A.; Vogel, E. *Angew. Chem.* **1973,** *85*, 585.
(13) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.*, **1980,** *102*, 683.
(14) For comparison the ^{13}C chemical shifts of C(1), C(6), and C(11) of the monocation **2** are 148.3, 127.8, and 40.8 ppm, respectively.
(15) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979,** *101*, 5537.
(16) For recent experimental and theoretical studies, see: (a) Bach, R. D.; Blanchette, P. E. *J. Am. Chem. Soc.* **1979,** *101*, 46. (b) Staral, J. S.; Yavari, I.; Roberts, J. D.; Prakash, G. K. S.; Donovan, D. J.; Olah, G. A. *Ibid.* **1978,** *100*, 8016. (c) Staral, J. S.; Roberts, J. D. *Ibid.* **1978,** *100*, 8018. (d) Olah, G. A.; Prakash, G. K. S.; Donovan, D. J.; Yavari, I. *Ibid.* **1978,** *100*, 7085. (e) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. K., Jr.; Murray, R. K. Jr. *Ibid.* **1978,** *100,* 1494.
(17) Olah, G. A.; Spear, R. J.; Hiberty, P. C.; Hehre, W. J. *J. Am. Chem. Soc.* **1976,** *98*, 7470.
(18) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975,** 97, 1539.
(19) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976,** *98*, 7333.
(20) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance in Organic Chemistry"; Pergamon Press: New York, 1969; Chapter 2, pp 98, 99.
(21) Kispert, L. D.; Engelman, C.; Dyas, C.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1971,** *93*, 6948.
(22) Weiss, R.; Priesner, C. *Angew. Chem.* **1978,** *90*, 484.
(23) Pagni, R. M.; Smith, R. J. *J. Am. Chem. Soc.* **1979,** *101*, 506.
(24) Smith, R. J., Pagni, R. M. *J. Am. Chem. Soc.* **1979,** *101*, 4769.
(25) From whom reprints may be obtained.

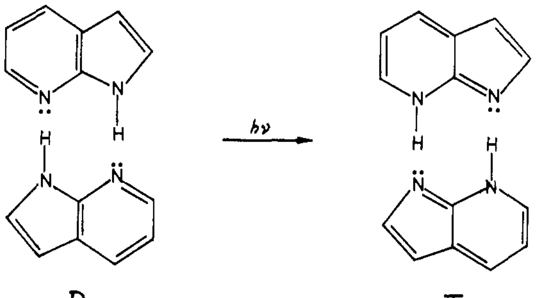
Koop Lammertsma, Hans Cerfontain*[25]
Laboratory for Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129
1018 WS Amsterdam, The Netherlands

Received November 26, 1979

Lack of Tunneling in the Excited-State Double Proton Transfer of 7-Azaindole Dimer?

Sir:

Hydrogen-bonded dimers of 7-azaindole (7-AI) undergo a photoinduced double proton transfer. The tautomeric form (T), stable in the excited state only, exhibits green, excimer-like fluorescence (F_2), red shifted by 10 000 cm^{-1} relative to the normal violet fluorescence (F_1). The dynamics of the cooperative two-proton transfer have been intensively studied.[1-5] Two mechanisms have been proposed. The first one is a thermal process where the two protons move over the energy barrier from high vibrational levels, populated according to a Boltzmann distribution. The second, a tunneling mechanism, has been postulated in order to explain the cooperative proton transfer (green fluorescence) observed at low temperatures, down to 4 K. Our results show that a tunneling mechanism is not necessary to account for the observed experimental effects.



D

T

Few data have been published concerning the triplet-state spectroscopy of 7-AI.[1] It is well known that the reactivities, especially acid-base properties, of molecules in the triplet state differ from those in the excited singlet state.[6] Moreover, the geometry of the triplet excimer formed from naphthalene was shown to be completely different from that in the fluorescent state.[7] The main task of our work was to find evidence for the existence of a tautomeric form of the dimer in the triplet state. By studying the phosphorescence and triplet ESR spectra we hoped to provide additional information on the mechanism for the cooperative two-proton transfer.

The procedure for measuring of luminescence and triplet ESR spectra were described elsewhere.[8] In the ESR measurements the triplet state was populated by continuous irradiation with a HBO-200 high pressure Hg lamp filtered through 5 cm of H_2O and a UG 11 Iena glass filter, containing mainly 313- and 302-nm Hg line groups. Concentrated solutions (10^{-3}-10^{-2}M) of 7-AI have been used. Relatively strong ESR signals were observed in alcohols and in aqueous-alcoholic solutions where the dimerization does not occur. In 3-methylpentane (3-MP) solutions where the dimerization is very efficient[3] the $\Delta m = \pm 1$ signals were extremely weak; only "$\Delta m = \pm 2$" transitions could be measured. The zero-field splitting (ZFS) parameters remained constant upon changing solvents and concentrations (see Table I). Our attempt to find

Table I. Zero-Field Splitting Parameters and Triplet Lifetimes of 7-Azaindole in Various Solvents at 77 K

solvent	C, M[a]	±0.001 cm^{-1} D^*"$_{\Delta m=2}$"	±0.0005 cm^{-1} $\lvert D\rvert$	$\lvert E\rvert$	±0.2 s τ_{ESR}	τ_{phosph}
3-methylpentane	1×10^{-2}	0.123			3.0	3.0
3-methylpentane	1×10^{-3}	0.124			3.1	3.1
1-propanol	1×10^{-3}	0.123	0.0919	0.0465	2.9	3.0

[a] Concentrations measured at room temperature.

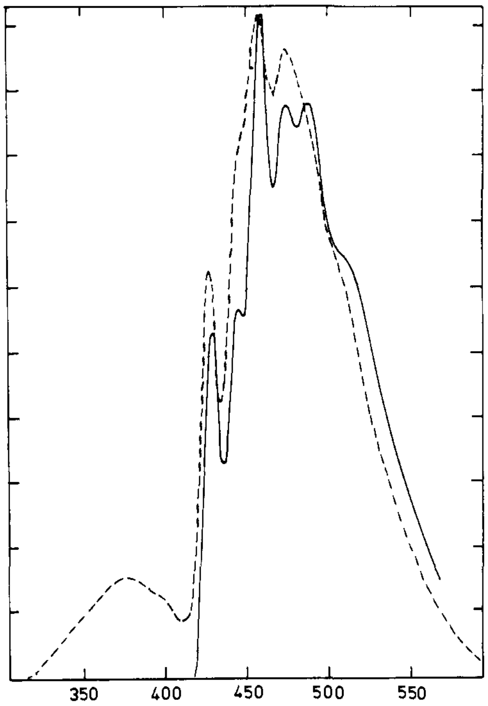


Figure 1. Solid curve: phosphorescence spectrum of 7-AI, 10^{-2} M in 3-MP at 77 K, excited at 313 nm using front surface excitation, corrected for spectral response (present work). Dashed curve: uncorrected fluorescence spectrum of 10^{-2} M solution of 7-AI in 3-MP excited at 285 nm (published in ref 3).

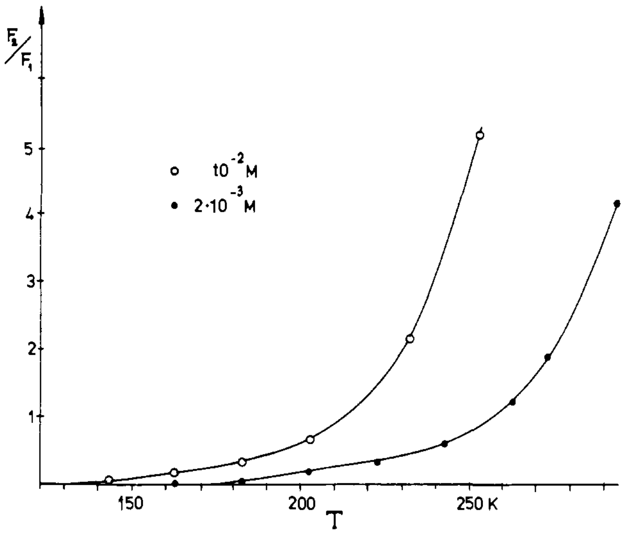


Figure 2. Effect of temperature on the F_2/F_1 ratio of 7-AI in 3-MP excited at 313 nm, using right-angle excitation. Intensities measured at the maxima of the corresponding bands (480 and 354 nm).

and select the second species, corresponding to the tautomeric form, failed. The phosphorescence spectrum was measured by the use of a chopper with a frequency of ~4 kHz. The same solutions as for ESR measurements have been used. Only one, well-structured spectrum (Figure 1) independent of solvents, concentration, and excitation wavelength has been observed. The following evidence excludes ascribing it to a delayed fluorescence: (1) the same lifetime, independent of observation wavelength, as that of the triplet ESR signal (see Table I); (2) appearance first at low temperatures (110 K in 3-MP) and an increase of intensity with lowering of temperature. In Figure 1 the low-temperature fluorescence published by El-Bayoumi is also reproduced for comparison. The energetic and vibronic similarities of the two spectra are astonishing. To elucidate this particular coincidence we have measured the temperature dependence of luminescence. The green fluorescence was unstructured down to 115 K. At 110 K we first observed the appearance of both vibronic structure and long-lived emission. We were unable to observe the fluorescence separately. The phase sensitive detector used by El-Bayoumi et al. also could not have achieved such a separation, despite their interpretation.[1-3] The existence of a structured, green fluorescence at low temperatures led those authors to infer a tunneling mechanism. *Our measurements show that, at low temperature, the tautomeric fluorescence is overlapped by the isoenergetic monomeric phosphorescence.* To test the postulated tunneling mechanism we have measured the temperature dependence of the fluorescence. Solutions (10^{-3}-10^{-2} M) of 7-AI in 3-MP have been excited by the 313-nm Hg line. Thus the dimeric species have been excited preferentially.[3] The F_2/F_1 ratio was determined by comparing the maxima of the corresponding bands, corrected for spectral response. In Figure 2 the F_2/F_1 ratio vs. temperature for two solutions of different concentration is shown. As one can see, the prominence of the tautomeric (F_2) fluorescence decreases upon lowering of temperature. Both curves in Figure 2 approach zero (the lowest value of F_2/F_1 ratio was 0.003) at temperatures where the phosphorescence was not yet observable. The lowest F_2/F_1 value reported by El-Bayoumi et al.,[3] 2.5 at low temperature, was interpreted as evidence of tunneling. However, the large value of the low-temperature plateau seems to be due to phosphorescence. Contrary to that, our results strongly suggest that the cooperative two-proton transfer proceeds via an activated process only (on excitation with the 313 nm). It is noteworthy that the energy dependence of the efficiency of tautomerization has been reported recently by Eisenthal et al.[9] They found also two different pathways for the generation of tautomer, and ascribed the slow component to thermally activated tautomerization rather than to tunneling.

It seems that the low-temperature experiments of El-Bayoumi et al.[2,3] inferring the tunneling need to be reinterpreted. There is not enough evidence to confirm the generally accepted tunneling mechanism of tautomerization.

Acknowledgment. The authors are grateful to Dr. Anna Grabowska for fruitful inspiration of the present work.[10]

References and Notes

(1) Taylor, C. A.; El-Bayoumi, M. A.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 253-260.
(2) Ingham, K. C.; Abu-Elgheit, M.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1971**, *93*, 5023-5025.
(3) Ingham, K. C.; El-Bayoumi, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 1674-1682.
(4) El-Bayoumi, M. Y.; Avouris, P.; Ware, W. R. *J. Chem. Phys.* **1975**, *62*, 2499-2550.
(5) Avouris, P.; Yang, Li. L.; El-Bayoumi, M. A. *Photochem. Photobiol.* **1976**, *24*, 211-216.

(6) Grabowski, Z. R.; Grabowska, A. *Z. Phys. Chem. (Frankfurt am Main)* **1976**, *101*, 197–208.
(7) Subudhi, P. C.; Lim, E. C. *Chem. Phys. Lett.* **1976**, *44*, 479–481.
(8) Bulska, H.; Chodkowska, A.; Grabowska, A. *J. Lumin.* **1979**, *20*, 39–49.
(9) Hetherington, W. M., III.; Micheels, R. H.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *66*, 230.
(10) This work was done under project 03.10.7. of the Polish Academy of Sciences.

Hanna Bulska,* Alina Chodkowska
Institute of Physical Chemistry
Polish Academy of Sciences, 01-224 Warsaw, Poland

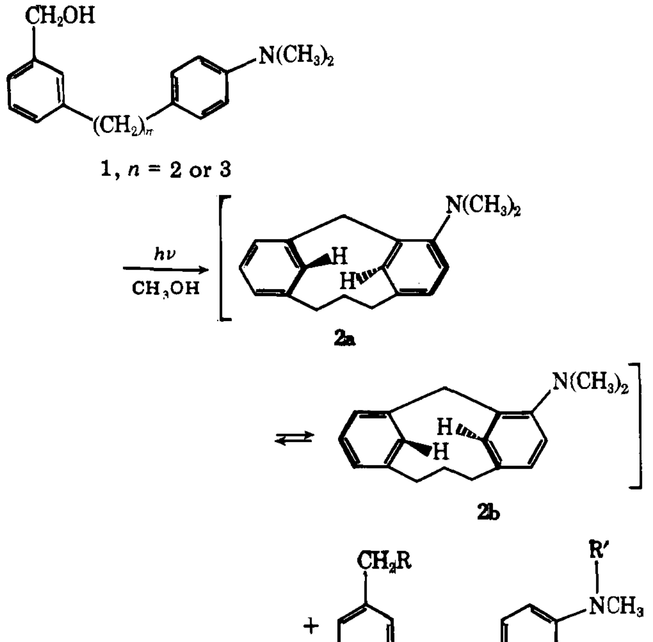
Received August 17, 1979

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

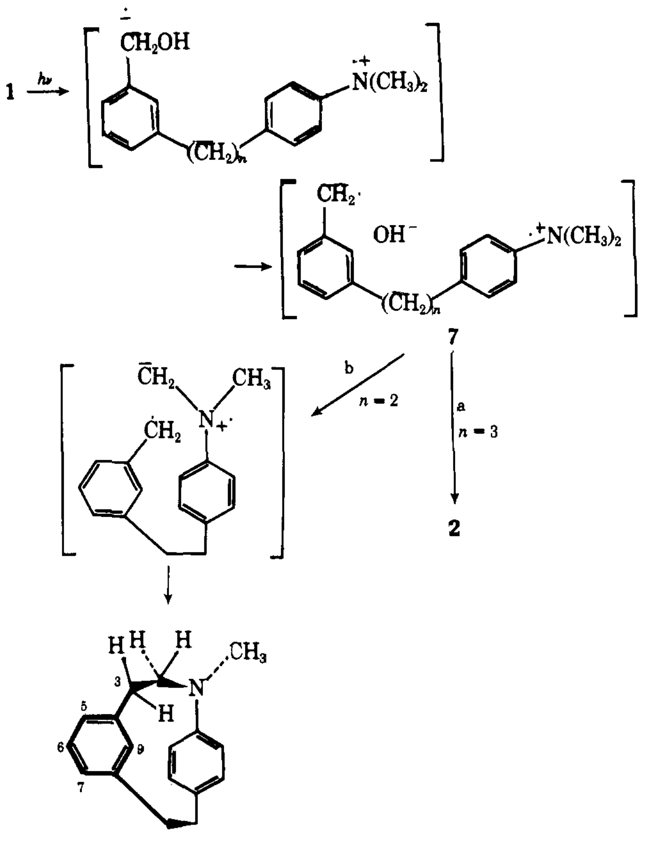
3, R = H; R′ = CH_3
4, R = OCH_3; R′ = CH_3
5, R = OCH_3; R′ = H

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-

Scheme I



6

0002-7863/80/1502-3261$01.00/0