tridendanyl unit a paramagnetic effect. In contrast, \( \text{I}b^3- \) exhibits pronounced diamagnetic ring currents along the periphery of the molecule.

Keywords: hydrocarbons · phenalenones · radicals · redox reactions


[3] The structure of 2 was confirmed unambiguously by X-ray analysis. Yellow needles of 2 suitable for X-ray structure analysis were grown by slow evaporation of a solution in CHCl₃ and n-hexane. Details of the structure will be reported in a separate paper.

[4] Decacyclene (Aldrich) was recrystallized from a xylene solution twice.

[5] Two regioisomeric tribromides could not be separated by column chromatography or recrystallization; however, this did not disrupt our synthesis, because we were converted to a single symmetrical product in the final steps, 10 to 1b^3-.

[6] Compounds 2–10 were fully characterized spectroscopically (\(^1\)H NMR, MS, IR).

[7] Neutral monoradical species \( \text{Ib}^1 \) and \( \text{Ic}^1 \) were stable in degassed toluene; their ESR signals did not change for a week at room temperature.


[9] Elemental analysis: found C 43.06, H 2.60%; calcd for C₃₇H₃₅N₂ (865.5): C, 38.58 H 3.66%; m.p. > 300 °C; UV/Vis (H₂SO₄): \( \lambda_{\text{max}} (\text{sh}) = 775(\text{sh}, 7760), 676(\text{sh}, 26700), 601(42500), 550(37900), 494(118000), 231 \text{nm (81800)} \).

[10] UV/Vis (THF): \( \lambda_{\text{max}} (\text{sh}) = 543(56300), 507(52300), 421(21000), 361(37300), 333(34300), 256 \text{nm (93000)} \).


[12] In phenalenyl derivatives the positions 1, 3, 4, 6, 7, and 9 are referred to as \( a \) and 2, 5, and 8 as \( b \). The shift changes (\( \Delta \alpha \)) are 51.8 at the \( a \) position and 4.9 at the \( b \) position. J. Sethorn, D. Johnels, E. Edlund, A. Sygula, J. Chem. Soc. Perkin Trans. 2, 1990, 1339.


An Intramolecular Base-Catalyzed Proton Transfer in 1,3-Bis(4-fluorophenyl)triazene

Ferdinand Männle and Hans-Heinrich Limbach*

Proton transfer processes are elementary steps in many acid- and base-catalyzed organic and biochemical reactions.\(^1\)\(^2\)\(^3\)\(^4\) Because of their complexity, simple model compounds are required if the proton motion is to be investigated experimentally, for example, by NMR spectroscopy or other fast reaction techniques. Model systems are also important for the theoretical treatment of proton transfers.\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\)\(^13\) Whereas several model systems for double proton transfer within or between neutral molecules have been devised,\(^11\)\(^12\)\(^13\) only a few model systems involving degenerate single proton transfer processes, which are coupled to charge transfer and therefore to solvent reorientation, are currently available. Recently, in the conjugated porphyrin monoanion\(^14\) an intramolecular single proton transfer that is characterized by a high activation barrier was observed. In contrast, the barrier for proton transfer is very low in hydrogen-bonded complexes formed by acetic acid and pyridine at low temperatures in organic solvents.\(^15\)\(^16\) Here we introduce a model system that lies between these two extremes: bis(4-fluorophenyl)\(\{1,3,15\}^3\)N\(_2\)triazene (1). The NMR experiments described below show that the intramolecular proton transfer in 1 occurs only in the presence of 2. Therefore, 2 acts as catalyst carrying the mobile proton of 1 from one nitrogen site to the other, as illustrated in Figure 1a.

The \(^1\)H NMR spectra of sealed samples of 1 in deuterated ethyl methyl ether that are carefully prepared with well-established vacuum techniques to exclude water and other acid or basic impurities do not show any sign of proton mobility. The partial room-temperature \(^1\)H NMR spectrum of such a sample is shown in Figure 2a. The signal of the mobile proton of 1 is split into a doublet by scalar coupling with a single \(^1\)N nucleus of 1 (\(J_{\text{NH}} = 93.5 \text{ Hz} \)), which indicates that the mobile proton is localized at a single nitrogen site. More precisely, potential

![Fig. 1. Proton transfer pathways for 1,3-bis(4-fluorophenyl)(1,3,15)N\(_2\)triazene (1): a) intramolecular proton transfer, catalyzed by trimethylamine; b) hypothetical intramolecular uncatalyzed proton transfer; c) intermolecular double proton transfer in hypothetical cyclic dimers of 1.](image-url)
intramolecular proton jumps (Fig. 1b), intermolecular double proton transfer in a hypothetical dimer (Fig. 1c), and intermolecular proton exchange catalyzed by impurities as discussed previously\(^{16-19}\) are slow on the NMR time scale. This also applies if a small amount of trimethylamine (2) is added before recording the spectrum at 137 K (Fig. 2c). Due to enhanced hydrogen bond formation the proton signal shifts to low field. However, if the temperature is increased to 248 K, a triplet can be observed, indicating a scalar coupling to both \(^{13}\)N atoms (\(J_{\text{HN}} = 47\) Hz). In the absence of 2 this doublet–triplet transition does not occur. The observation of this triplet verifies that a fast intramolecular proton transfer according to Figure 1a is mediated by 2. Intermolecular proton exchange would lead to a doublet–singlet transition.\(^{113}\) Since only one signal was observed for the mobile proton of 1, the hydrogen–bond exchange between solvated monomer 1 and its 1:1 complex with 2 is fast on the NMR time scale. The same proton therefore shuttles frequently between the two nitrogen sites of 1, whereas a different base molecule (2) catalyzes each jump. During the proton carrier process the proton must be temporarily transferred from 1 to 2—this creates a contact ion pair. The properties of the contact pair ensure that proton transfer to the initial or second nitrogen site of 1 is faster than the dissociation of the contact ion pair that would lead to intermolecular proton exchange. This finding is plausible, because the free energy of dissociation of the contact ion pair is enormous in a solvent with a low dielectric constant as a result of the Coulomb interaction. By contrast, the dissociation energy of the molecular 1:1 complex between 1 and 2 is minimal, leading to the fast hydrogen bond exchange mentioned above.

The uncatalyzed intramolecular proton transfer of 1 is understandably slow, since no intramolecular hydrogen bond is present. Furthermore, 1 does not form cyclic dimers in which a double proton transfer could take place according to Figure 1c, as is the case with the related diarylamidines.\(^{113}\) This observation can be rationalized, because 1 is planar, and the associated steric repulsion between the aromatic protons within a dimer hinders the approach of the two molecules and the formation of strong hydrogen bonds.

In conclusion, in an aprotic and not necessarily apolar solvent, bases such as trimethylamine are capable of picking up mobile protons at one molecular site and carrying them rapidly to another site. The transfer occurs faster than the dissociation of the intermediate contact ion pair. The system diaryltriazene/trimethylamine therefore is an interesting model for further experimental and theoretical studies of proton carrier processes, which could perhaps contribute to the understanding of the mechanisms of enzyme reactions.

**Keywords:** catalysis · NMR spectroscopy · proton transfer


Regioselective Palladium-Catalyzed Hydrostannylation of Unsymmetrical Oxabicyclic Alkenes**

Mark Lautens* and Wolfgang Klute

Hydrometallation reactions are widely used for the generation of stereochemically defined organometallic compounds. Transition metal catalysts have been shown to accelerate the hydroboration,\(^{11}\) hydroisilylation,\(^{12}\) and hydroalumination of alkenes.\(^{13}\) Significant control of the regio-, stereo-, and enantioselectivity has been achieved.

[*] Prof. M. Lautens, Dr. W. Klute
Department of Chemistry, University of Toronto
Toronto, Ontario M5S1A1 (Canada)
Fax: Int. code +416/978-6083
e-mail: mlautens@alchem.chem.utoronto.ca

[**] M. L. thanks NSERC (Canada) for support of this work in the form of an E. W. R. Steacie Fellowship. W. K. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

**Keywords:** catalysis · NMR spectroscopy · proton transfer

Received: November 17, 1995 [Z56511E]
German version: Angew. Chem. 1996, 108, 477–479