Coexistence of Two Triplets for the Twisted Intramolecular Charge Transfer (TICT) Probe 4-(Dimethylamino)benzonitrile in Polar Solvents: An Experimental Evidence

by **Nitin Chattopadhyay**[1])*, **Carlos Serpa**, **Luis G. Arnaut**, and **Sebastião J. Formosinho**

Department of Chemistry, Coimbra University, P-3049 Coimbra (e-mail : pcnitin@yahoo.com)

Room-temperature nanosecond/microsecond laser-flash photolysis and low-temperature phosphorescence studies reveal that two different triplets coexist during the twisted intramolecular charge transfer (TICT) of 4-(dimethylamino)benzonitrile in polar solvents.

Introduction. – The dual luminescence of 4-(dimethylamino)benzonitrile (DMABN) and related molecular systems in solution, discovered in the early sixties [1], has received immense attention due to its application in diverse fields including laser dyes, isomerization of polyenes and rhodopsin, molecular switching devices, and charge separation in photochemical-energy utilization [2–5]. Because of its simple molecular architecture, DMABN has been used as the prime molecular system for such studies since the discovery of this phenomenon, although other systems are now being investigated increasingly [5–24]. Among the several mechanisms proposed by several groups to explain the phenomenon [7–15], the most widely accepted mechanism, first put forward by *Grabowski* and co-workers [13–15], proposes that the fluorophore, upon excitation, undergoes an intramolecular charge transfer (ICT) from the donor Me_2N group to the acceptor CN part *via* the benzene ring, accompanied by a twisting of the former group to a conformer nearly perpendicular to the benzene plane. Although, the phenomenon has been studied widely in the S_1 state of the fluorophore in homogeneous and microheterogeneous solutions [5–15], interestingly, there are only few reports on the corresponding triplets [8][18–22]. From their laser-flash photolysis and EPR measurements, *Köhler et al.* inferred that the lowest triplet of DMABN and other related compounds is generally a non-charge-transfer (non-CT) state, irrespective of the solvent polarity, although they observed a significant solvent effect on the T-T absorption spectra [19] in terms of the relative intensities of the two bands. From their semi-empirical calculations, *Majumdar et al.* [23] and *Purkayastha et al.* [24] also showed that the lowest triplet state of DMABN is of $\pi\pi^*$ nature. However, *Hashimoto* and *Hamaguchi*, by means of their nanosecond time-resolved IR spectroscopy, identified two distinct triplet species for DMABN in solvents of different polarity [20]. They ascribed the 2000-cm^{-1} band in nonpolar solvents to the non-CT (or locally exited (LE)) triplet and the 2040-cm^{-1} band in BuOH to the CT triplet. In spite of the fact that, in the polar solvents, they could detect the signal corresponding to only one

---

[1])   Permanent address: Department of Chemistry, Jadavpur University, Calcutta-700032, India.

triplet, which they ascribe to the twisted intermolecular charge transfer (TICT) triplet, the authors argued in favor of an equilibrium between the TICT and LE triplets in polar solutions.

In this paper, we present experimental evidence for the coexistence of two triplets for DMABN in polar solutions from our room-temperature nanosecond/microsecond flash photolysis and low-temperature phosphorescence studies.

Results and Discussion. – Flash photolysis of a $1.2 \cdot 10^{-5}$ M solution of DMABN in isopentane and in heptane yielded a T-T absorption spectrum consisting of two bands similar to that observed by others [18][19]. The stronger band has a maximum at around 370 nm, while the week one is quite broad and spans around 480–520 nm. In polar solvents like MeOH or MeCN, the DMABN solution yielded T-T absorption spectra with two bands principally similar to those observed in alkane environments. Since, in all the solvents, both bands decay at the same rate (*Fig. 1*) and are quenched by oxygen uniformly, we assign the whole spectrum to the triplet-triplet (T-T) absorption of DMABN. However, we observed a red shift in the spectral position in the polar environments (*Fig. 1*). In both MeOH and MeCN, the T-T absorption bands have maxima at *ca.* 390 and 550 nm. It is pertinent here to point out that our resolution of the experiment may ignore a further small shift from MeOH to MeCN, as we measured the absorption at 10 nm intervals. However, the gradual shift of the T-T absorption spectrum was further confirmed when we got the maxima of the bands at *ca.* 380 and 530 nm in tetrahydrofuran (THF), a solvent with a polarity between alkanes and MeOH (not included in *Fig. 1*, for clearness). We ascribe the shift in the T-T absorption spectra in different solvents to the polarity effect of the environment.

We analysed the decays of the triplet-triplet absorption signals in different solvents over the entire spectral region. In isopentane, it was found to be single-exponential
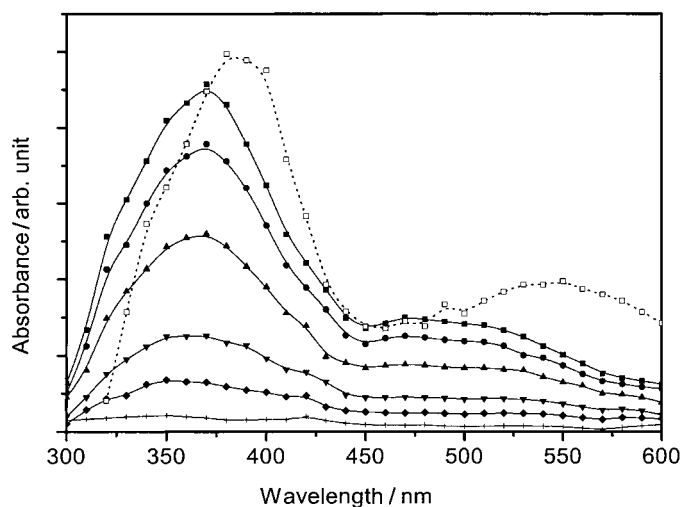

Fig. 1. *Room temperature triplet-triplet absorption spectra of DMABN in isopentane* (■, ●, ▲, ▼, ♦) *and MeCN* (□): *Time after laser flash: 1 μs* (□, ■), *3 μs* (●), *8 μs* (▲), *18 μs* (▼), *25 μs* (♦), *and 60 μs* (+).

yielding a lifetime of 10 ± 1 µs at room temperature (*Fig. 2*). The observation was similar in heptane with a similar lifetime of the triplet. A single-exponential decay is compatible with the presence of only one triplet in the nonpolar environments. This is consistent with the idea that, in nonpolar solvents, only the LE form exists, and the TICT does not form for both thermodynamic (the TICT state is higher in energy than the LE state) as well as kinetic (high activation barrier) reasons [2–4].
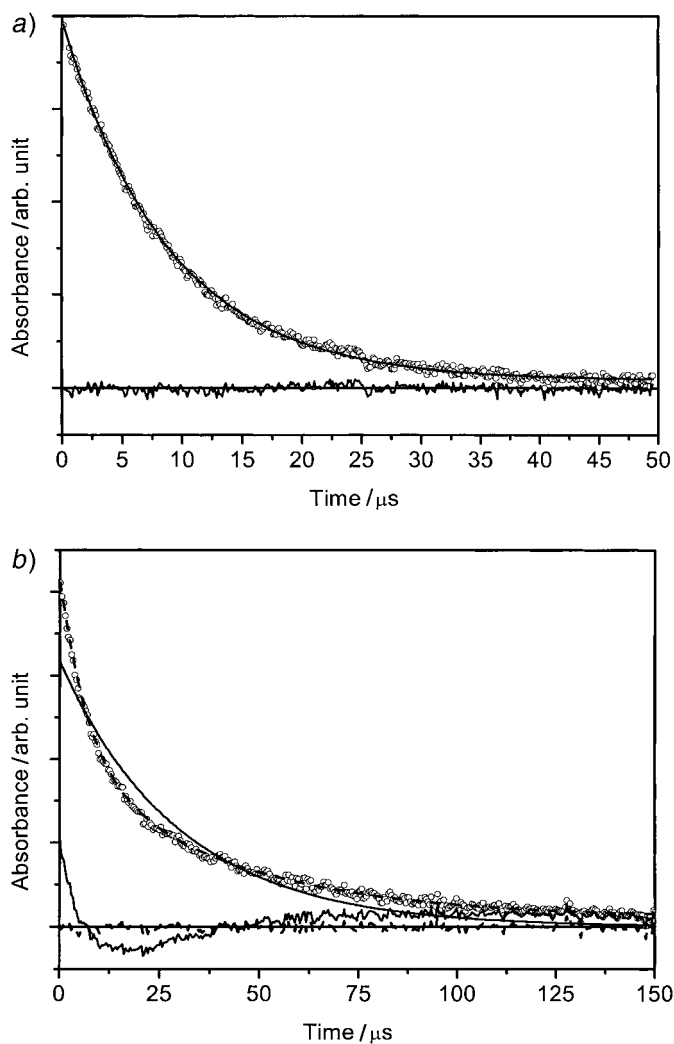

Fig. 2. *Triplet decay of DMABN at room temperature obtained from flash photolysis* ($\lambda_{exc.}$ 266 nm, $\lambda_{abs.}$ 380 nm) *in* a) *isopentane and* b) *MeCN*. ○ = experimental data points; solid lines represent the *single*-exponential fits and the broken line the *double*-exponential fit. The bottom parts represent the residuals (solid and the broken lines correspond to the *single*- and the *double*-exponential fits, resp.).

Interestingly, however, the decays in the polar solvents were bi-exponential (*Fig. 2*). Deviation from the mono-exponential character of the decays increased with an increase in the solvent polarity. This indicates an enhancement of the population of the short-lived triplet (supposed to correspond to TICT, *vide supra*) in a more polar environment, which is consistent with the existing idea that TICT is favored in more polar media. The possibility that the short-lifetime component can be due to T-T annihilation is ruled out from the fact that it would have been equally favored in alkane environments, also as the concentration of the solutions are the same. The mono-photonic ionization under the experimental conditions is negligible [25]. The possibility of biphotonic photodegradation of the probe is also ruled out from the fact that the transient absorption spectra as well as the decay times were independent of the laser intensity in the range of our experimental conditions. Constancy of the absorption as well as of the fluorescence spectra of the solution before and after flash photolysis rules out the possibility of formation of any photochemical product. Analysis of the decay at room temperature over the entire spectral range gave two lifetimes, *i.e.* as 5.5 ± 0.5 and 30 ± 2 μs and 8.8 ± 0.8 and 42 ± 3 μs in MeOH and MeCN, respectively. Unfortunately, there is no appropriate data available for the triplet lifetime of DMABN at room temperature to compare with our experimental values. *Hashimoto* and *Hamaguchi* reported that in polar solvent (BuOH) at room temperature, the DMABN triplet decayed in the submicrosecond time scale [20] although they did not specify any value. *Köhler et al.* [19] reported the lifetime of the triplet of another similar molecular system, *viz.*, 4-(dimethylamino)-2-methylbenzonitrile, in the lower milli-second ranges in highly viscous alcoholic environments in the low-temperature range -74 to $-97°$. The present experimental values of the lifetimes of the DMABN triplets at room temperature, thus, sound reasonable compared with the above-mentioned reports available. The bi-exponential nature of the decays in the polar solvents clearly reveals that two different triplets coexist in the polar media, in contrast to a single triplet in the nonpolar environment. We tentatively assign these two triplets to the locally excited (LE) and the TICT forms. Since TICT of DMABN does not take place in nonpolar media [2 – 5][23], we assign the triplet in alkane solvents to the triplet of the LE form. In polar solvents like MeOH and MeCN, TICT takes place, resulting in two triplets in these solvents, corresponding to the LE and the TICT forms of DMABN. In concurrence with our phosphorescence study (see below), we assign the short-lived triplet to the TICT form. The lifetime of the LE triplet was found to depend on the solvent and increased with an increase in the polarity. To ascertain this, we extended our room temperature flash study of the same probe to the THF solvent of intermediate polarity, and the triplet lifetime 21 ± 2 μs was obtained. Thus, a gradual increase in the LE triplet lifetime with an increase in the solvent polarity confirms that the longer-lived triplet in MeOH and MeCN corresponds to the LE triplet. The gradual increase in the triplet lifetime with an increase in the solvent polarity is explained as follows. The lowest triplet state of DMABN has been shown to be a $\pi\pi^*$ state [23][24] and the relaxed triplet is known to be less polar than the ground-state ($\mu_{T_1}^{calc.} = 3.84$ D and $\mu_{S_0}^{calc.} = 5.22$ D)[2]) [23]. This suggests that with an increase in the solvent polarity, the

---

[2])   Some of the reported values of μ_{S_0} are: 5.22 D [23], 5.35 D [24], 6.6 D [8], and 7.78 D [17]. However, in [23], the dipole moment of the geometrically optimized triplet state is reported to be 3.84 D.

energy gap between the lowest triplet and the ground-state increases. As per the energy-gap law, this leads to a decrease in the transition from the lowest triplet to the ground state, resulting in an enhancement in the triplet lifetime.

We were unable to resolve the spectra corresponding to a single triplet species. However, to get an impression of the relative population of the two triplets over the different regions of the T-T absorption spectrum in MeCN (where TICT is supposed to be most prominent), we plotted the ratio of the pre-exponential terms corresponding to the two lifetimes as obtained from the bi-exponential analyses against wavelength in the range 350–490 nm. A good linearity with a small negative slope reflects that the entire spectral envelope consists of the absorption from both the triplets, the TICT triplet (with shorter lifetime) being slightly more abundant at the higher-energy side of the envelope. The present proposition seems resonable as the benzonitrile radical anion (which is nearly analogous to the TICT form of DMABN) in aqueous solution has a strong absorption band at 315 nm (ε 25400) and a week band at 410 nm (ε 4700) [26].

To substantiate the results from the room temperature flash-photolysis experiments, we performed phosphorimetric studies of the molecular system in nonpolar as well as polar glassy matrices at 77 K. In the frozen matrices, the intramolecular twisting is restricted. So, we allowed the liquid solution to be excited under an excitation source and froze the mass in a photostationary state. Actually, the solutions were frozen separately in the presence as well as in the absence of the exciting light. There was no substantial difference between the phosphorescence spectra of DMABN in isopentane or in MeOH glass frozen in the presence or absence of the exciting light. Analysis of the phosphorescence decays in the two matrices frozen under different conditions of excitation, however, yielded interesting results. In the isopentane matrix, the phosphorescence decay was single-exponential, irrespective of the irradiation condition at the time of freezing, and the phosphorescence lifetime was determined to be 1.6 ± 0.2 s. In MeOH glass, the decay was single-exponential only when the solution was frozen in the dark (in the absence of the excitation source), giving a triplet lifetime of 2.2 ± 0.2 s in the frozen matrix. We believe that, in these two situations, the triplet corresponds to the LE form as the TICT form does not exist in the ground-state [2–4][23]. When the MeOH solution was frozen under irradiation, the phosphorescence decay turned to have a clear bi-exponential character (*Fig. 3*). Analysis of the decay resulted in two lifetimes, *i.e.* 2.4 ± 0.2 and 0.25 ± 0.1 s. The MeOH glass, frozen under illumination and leading to the bi-exponential decay, was allowed to melt to the liquid state, and the same solution was then refrozen, but now in the absence of light. This time, we got a single-exponential decay with a decay time similar to the long one in the previous study. Generation of any photoproduct responsible for the short decay is, thus, ruled out.

We assign the component with a lifetime close to that in the isopentane matrix as well as in MeOH glass (the latter frozen in the absence of exciting light) to the triplet of the LE form as under these conditions, TICT does not exist, while the short-lived triplet is attributed to the TICT form. We believe that the TICT and the LE triplets are in equilibrium in the polar solvents, in agreement with *Hashimoto* and *Hamaguchi* [20]. Trapping of the photostationary state by different means like freezing and crystallization is now well-established in organic photochemistry [27–29]. A variation in the high-frequency magic-angle spinning ^{1}H-NMR spectral pattern for 2-(2,4-dinitroben-
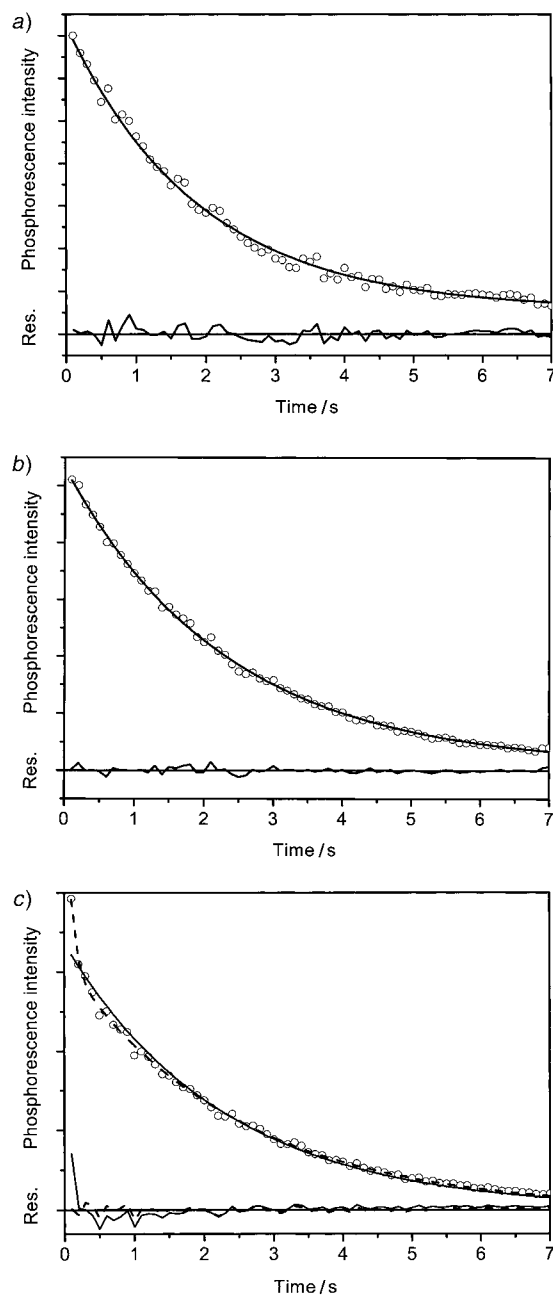
Fig. 3. *Phosphorescence decay of DMABN* ($\lambda_{exc.}$ 266 nm, $\lambda_{emission}$ 420 nm) *at 77K in* a) *isopentane and* b), c) *MeOH glass.* ○ = experimental data points, the solid and the broken lines are the *single-* and *double-* exponential fits. The bottom parts represent the residuals. The MeOH solution was frozen in the absence of exciting light for *b*) and in the presence of exciting light for *c*). In isopentane (see *a*)), the decays were identical, irrespective of the presence or absence of exciting light. For details, see text.

zyl)pyridine, recrystallized from solution in the presence and absence of UV radiation led *Nunes et al.* to propose that the photostationary state for the excited state intramolecular proton-transfer process was trapped [27]. The photostationary state for the dimerization of 9-substituted anthracenes to form head-head and head-tail dimers in the molten state in the presence of light was frozen by *Schmidt* [28]. A similar trapping of the photostationary state during the *cis/trans* photoisomerization of tetrathiafulvalenenaphthalenophanes has also been reported by *Ballardini et al.* [29].

Experimental Part

General. DMABN was purified by vacuum sublimation and repeated crystallization from EtOH. All the solvents (from *Aldrich*), *viz.*, isopentane, heptane, THF, MeOH, and MeCN were of spectroscopic grade and used as received after verifying their transparency by blank fluorescence, phosphorescence, and flash experiments.

Flash Phololysis. Our flash photolysis setup is comprised of a *Spectra-Physics Quanta-Ray GCR-130* Nd-YAG laser, an *Applied Photophysics LKS-60* laser flash photolysis spectrometer, and a *Hewlett-Packard Infinium* oscilloscope (500 MHz, 1 Gsa/s). The samples were excited with the fourth harmonic (266 nm) of the laser. The monitoring light was produced by a 150-W pulsed Xe lamp. The detection of the transient species in the range 300–600 nm was made with a *Hamamatsu* photomultiplier (*1P-28*). As the T-T absorption signals at r.t. were found to be very sensitive to oxygen quenching, the sample solns. were carefully degassed with Ar in a specially designed cell for ½ h prior to their use in the flash experiments.

Phosphorescence. The phosphorescence studies were performed with a *SPEX Fluorolog-3* spectrofluorimeter with the *1934D4* module for phosphorimetry. Wherever necessary (*vide infra*), we excited the fluid soln. with a Hg-vapour lamp (*Applied Photophysics*; 125 W) through the other window of the sample chamber and froze the soln. by pouring liq. N_2 under photolytic equilibrium. The external light source was removed after complete freezing.

REFERENCES

[1] E. Lippert, W. Lüder, H. Boos, in 'Advances in Molecular Spectroscopy', Ed. A. Mangini, Pergamon Press, Oxford, 1962, p. 443.
[2] E. Lippert, W. Rettig, V. Bonacic-Koutecký, F. Heisel, J. A. Miehe, *Adv. Chem. Phys.* **1987**, *68*, 1.
[3] W. Rettig, *Angew. Chem., Int. Ed.* **1986**, *25*, 971.
[4] K. Bhattacharyya, M. Chowdhury, *Chem. Rev.* **1993**, *93*, 507.
[5] S. Kundu, S. C. Bera, N. Chattopadhyay, *Indian J. Chem., Sect. A* **1998**, *37*, 102.
[6] S. Kundu, S. Maity, S. C. Bera, N. Chattopadhyay, *J. Mol. Struct.* **1997**, *405*, 231, and ref. cit. therein.
[7] U. Leinhos, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem.* **1991**, *95*, 2013.
[8] W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem.* **1992**, *96*, 10809.
[9] Y. V. Il'ichev, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem. A* **1998**, *102*, 5670.
[10] R. J. Visser, P. C. M. Weisenborn, P. J. M. van Kan, B. H. Huizer, C. A. G. O. Varma, J. M. Warman, M. P. De Hass, *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 689.
[11] P. C. M. Weisenborn, C. A. G. O. Varma, M. P. De Hass, J. M. Warman, *Chem. Phys. Lett.* **1986**, *129*, 562.
[12] Y. Wang, M. McAuliffe, F. Novak, K. B. Eisenthal, *J. Phys. Chem.* **1981**, *85*, 3736.
[13] K. Rotkiewicz, K. H. Grellmann, Z. R. Grabowski, *Chem. Phys. Lett.* **1973**, *19*, 315.
[14] K. Rotkiewicz, K. H. Grellmann, Z. R. Grabowski, *Chem. Phys. Lett.* **1973**, *21*, 212.
[15] J. Karpiuk, Z. R. Grabowski, F. C. De Schryver, *Proc. Indian Acad. Sci.* **1992**, *104*, 133.
[16] A. B. J. Parusel, G. Köhler, S. Grimme, *J. Phys. Chem. A* **1998**, *102*, 6297.
[17] A. B. J. Parusel, *Phys. Chem. Chem. Phys.* **2000**, *2*, 5545.
[18] Y. Wang, *J. Chem. Soc. Farad. Trans. 2* **1988**, *84*, 1809.

[19] G. Köhler, G. Grabner, K. Rotkiewicz, *Chem. Phys.* **1993**, *173*, 275.
[20] M. Hashimoto, H. Hamaguchi, *J. Phys. Chem*. **1995**, *99*, 7875.
[21] N. Chattopadhyay, J. Rommens, M. Van der Auweraer, F. C. De Schryver, *Chem. Phys. Lett.* **1997**, *264*, 265.
[22] N. Chattopadhyay, M. Van der Auweraer, F. C. De Schryver, *Chem. Phys. Lett.* **1997**, *279*, 303.
[23] D. Majumdar, R. Sen, K. Bhattacharyya, S. P. Bhattacharyya, *J. Phys. Chem.* **1991**, *95*, 4324.
[24] P. Purkayastha, P. K. Bhattacharyya, S. C. Bera, N. Chattopadhyay, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3253.
[25] G. Köhler, N. Getoff, K. Rotkiewicz, Z. R. Grabowski, *J. Photochem*. **1985**, *28*, 537.
[26] B. Chutný, A. J. Swallow, *Trans. Faraday Soc*. **1970**, *66*, 2847.
[27] T. Nunes, Y. Eichen, M. Bastos, H. D. Burrows, H. P. Trommsdorff, *J. Phys. D: Appl. Phys.* **1999**, *32*, 2108.
[28] G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647.
[29] R. Ballardini, V. Balzani, J. Becher, A. D. Fabio, *J. Org. Chem*. **2000**, *65*, 4120.