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Avenues into the Synthesis of Illusive Poly(*m*-phenylene-*alt*-squaraine)s: Polycondensation of *m*-Phenylenediamines with Squaric Acid Intercepted by Intermediate Semisquaraines of Exceptionally Low Reactivity

Marco A. Balbo Block, Anzar Khan, and Stefan Hecht*

Institut für Chemie/Organische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany

shecht@chemie.fu-berlin.de

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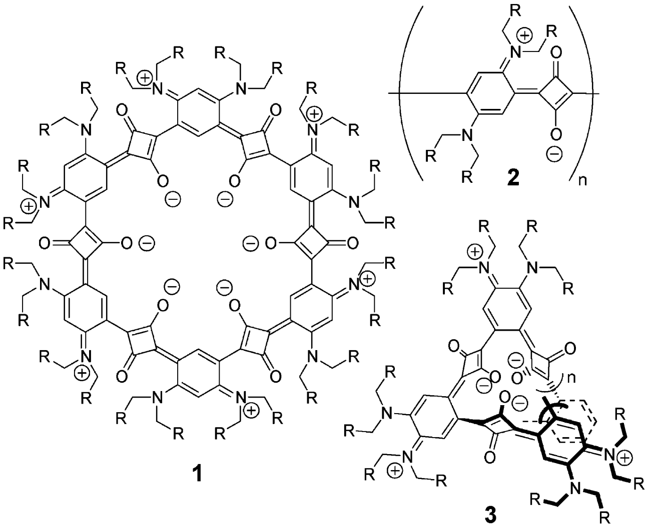
Abstract: The synthesis and properties of a novel class of *ortho*-dialkylamino-substituted semisquaraines are described. The exceptionally low reactivity of the investigated compounds is caused by an intramolecular hydrogen bond as evidenced by experimental and computational studies. Although this constitutes the reason for our failed attempts to prepare poly(*m*-phenylene-*alt*-squaraine)s, the discovered influence of hydrogen bonding on the photophysical properties of these semisquaraines provides a promising new motif for sensor design.

Introduction

Squaraine dyes[1] are well-known for their exceptional properties,[2] including their relatively small HOMO−LUMO gaps, high extinction coefficients, photoconductivity, and net charge neutrality, that have been exploited in a number of applications. The incorporation of the squaraine chromophore into a conjugated framework promises improved properties due to the predicted low band gaps[3] and polymer processibility. Therefore, to access intrinsically conducting as well as IR-emitting polymers based on donor−acceptor substituted conjugated polymers,[4] poly(squaraine)s[5] have received considerable attention.[6] In all cases, the polymers have been accessed via a standard $A_2 + B_2$ polycondensation route involving squaric acid as the biselectrophile and an electron-rich aromatic or bisenamine moiety as the bisnucleophile.[7,8] However, the prepared polymers, mostly of the poly(pyrrole-*alt*-squaraine) type,[7] exhibit relatively low degrees of polymerization and poor solubility, contain regiodefects arising from β-substitution, and allow for only limited architectural control.

CHART 1



Our interest in this field originates from the idea of utilizing phenylenediamine derivatives to obtain poly(phenylene-*alt*-squaraine)s of various topologies such as rodlike, cyclic, and helical structures **1**−**3** (Chart 1), respectively, depending on the employed regioisomer, i.e., *o*-, *m*-, or *p*-phenylenediamine. Due to their expected advantageous photophysical properties[3] and the readily tunable substitution to introduce, for instance, solubilizing groups, these compounds would be promising candidates for optoelectronic, sensory, and transport applications. Here, we report on our attempts toward the synthesis of poly(*m*-phenylene-*alt*-squaraine)s and subsequently performed experiments devoted to understand the unusual reactivity of intermediate phenylenediamine−squaric acid monoadducts. We focus on the case of *m*-phenylenediamines as activated aromatic moieties since both amino substituents donate electron density to the same carbon centers leading to a strong directing effect, thereby affording *meta*-linked chain segments that

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(1) (a) Treibs, A.; Jacob, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 694−695. (b) A review is given in: Schmidt, A. H. *Synthesis* **1980**, 961−994.

(2) For reviews, consult: (a) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449−486. (b) Das, S.; Thomas, K. G.; George, M. V. *Mol. Supramol. Photochem.* **1997**, *1*, 467−517. (c) Law, K.-Y. *Mol. Supramol. Photochem.* **1997**, *1*, 519−584.

(3) (a) Brocks, G.; Tol, A. *J. Phys. Chem.* **1996**, *100*, 1838−1846. (b) Brocks, G.; Tol, A. *Synth. Met.* **1996**, *76*, 213−216.

(4) For a review, see: van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *R32*, 1−40.

(5) For a recent review, consult: Ajayaghosh, A. *Chem. Soc. Rev.* **2003**, *32*, 181−191.

(6) Representative reviews on conjugated polymers and their use in organic electronics are given in: (a) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402−428. (c) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359−369. (d) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117. (e) Rogers, J. A.; Bao, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3327−3334.

(7) (a) Treibs, A.; Jacob, K. *Liebigs Ann. Chem.* **1966**, *699*, 153−67. (b) Lynch, D. E.; Geissler, U.; Peterson, I. R.; Floersheimer, M.; Terbrack, R.; Chi, L. F.; Fuchs, H.; Calos, N. J.; Wood, B.; Kennard, C. H. L.; Langley, G. J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 827−832. (c) Lynch, D. E.; Peterson, I. R.; Floersheimer, M.; Essing, D.; Chi, L.-F.; Fuchs, H.; Calos, N. J.; Wood, B.; Kennard, C. H. L.; Langley, G. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 779−784. (d) Lynch, D. E.; Geissler, U.; Calos, N. J.; Wood, B.; Kinaev, N. N. *Polym. Bull.* **1998**, *40*, 373−380. (e) Ajayaghosh, A.; Chenthamarakshan, C. R.; Das, S.; George, M. V. *Chem. Mater.* **1997**, *9*, 644−646. (f) Chenthamarakshan, C. R.; Ajayaghosh, A. *Chem. Mater.* **1998**, *10*, 1657−1663. (g) Chenthamarakshan, C. R.; Eldo, J.; Ajayaghosh, A. *Macromolecules* **1999**, *32*, 251−257.

(8) (a) Chen, Y. Y.; Hall, H. K., Jr. *Polym. Bull.* **1986**, *16*, 419−425. (b) Havinga, E. E.; Ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119−126. (c) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55*, 299−306. (d) Havinga, E. E.; Pomp, A.; Ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1995**, *69*, 581−582. (e) Ajayaghosh, A.; Eldo, J. *Org. Lett.* **2001**, *3*, 2595−2598. (f) Eldo, J.; Ajayaghosh, A. *Chem. Mater.* **2002**, *14*, 410−418.

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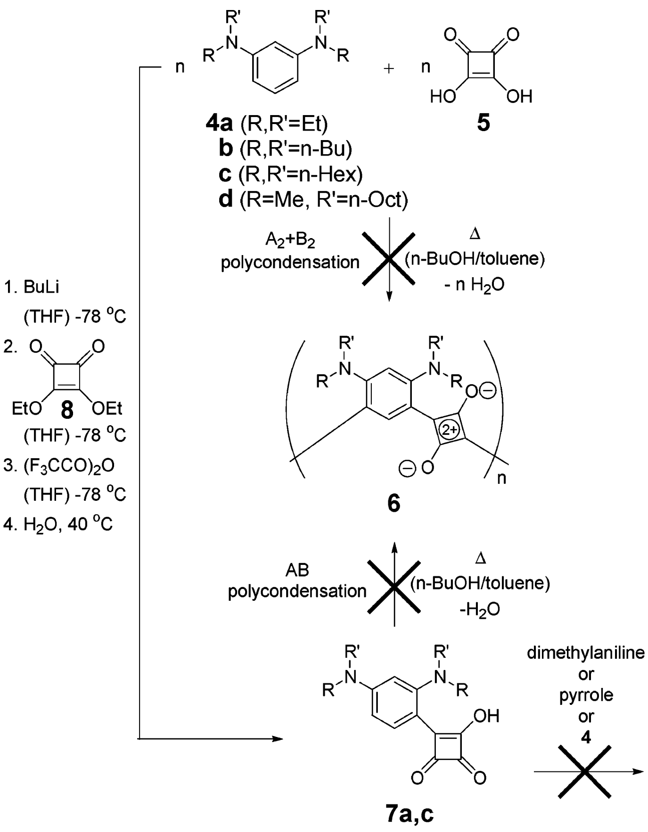
SCHEME 1



encode oligomeric macrocycles and polymeric helices as targets of our interest.

Results and Discussion

Polycondensation. Tertiary *m*-phenylenediamines **4a**−**c** were readily accessible by standard alkylation and reductive amination protocols, respectively.[9] The asymmetrically substituted derivative **4d** was prepared via a three-step amidation, N-alkylation, reduction sequence. It should be noted that tertiary amines have to be employed in squaraine condensations to prevent competing squaramide formation. With these bifunctional monomers in hand, $A_2 + B_2$ polycondensation reactions with squaric acid **5** were carried out (Scheme 1). However, employing various conditions, i.e., dehydrating agents (e.g., tributyl orthoformate), solvents (e.g., *n*-butanol/toluene mixtures, DMSO), and temperatures (e.g., 110−180 °C), only short ($2 \leq n \leq 5$), highly colored oligomers **6** were formed according to GPC[9] as well as MALDI-TOF MS analysis.

The observed low degrees of polymerization indicate inefficient elementary condensation steps. To investigate the polycondensation limiting step, semisquaraines **7a**,**c** resembling key intermediates (AB monomers) in the polycondensation process were prepared and their reactivities studied.

Semisquaraine Model Studies. Two semisquaraines **7a**,**c** were synthesized using a newly developed three-step sequence involving lithiation of tertiary phenylenediamines **4a**,**c** and coupling with diethyl squarate **8** followed by hydrolysis[10] to afford **7a**,**c** in moderate yields (Scheme 1).[9] Detailed characterization was performed, including ^1H and ^{13}C NMR, EI-HRMS, IR, UV/vis, and emission spectroscopy, while purity was confirmed by HPLC. To our knowledge, these compounds are the first reported semisquaraines carrying *ortho*-dialkylamino substituents. Semisquaraines **7a**,**c** serve as ideal model compounds since they potentially contain both electrophilic (semisquaraine carbonyl) and nucleophilic (electron-rich aromatic) sites and therefore resemble AB monomers. Surprisingly, even under vigorous conditions (vide supra), self-condensation (AB polycondensation) could not be affected, indicating a lack of reactivity on one or both sites. The phenylenediamine system is significantly deactivated by the introduction of the squaric acid moiety. This is indicated by the downfield ^1H NMR shifts of the aromatic ring protons in **7a** as compared to **4a** (Figure 1).

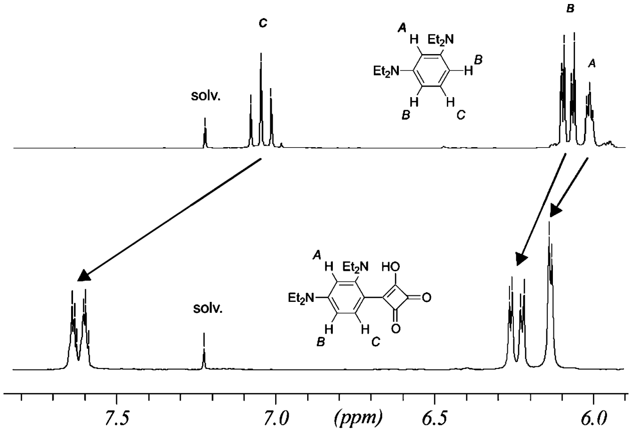


FIGURE 1. ^1H NMR comparison of the aromatic region before (**4a**, top) and after (**7a**, bottom) introduction of the squaraine moiety to the *m*-phenylenediamine system (solvent: $CDCl_3$).

Interestingly, also the electrophilic character of the investigated semisquaraines **7a**,**c** is greatly diminished since virtually no reaction took place with highly active aromatic systems such as *N*,*N*-dimethylaniline, pyrrole, and phenylenediamine **4c** to give the expected squaraine dimers. Even under extremely forcing conditions involving reflux in *n*-butanol/toluene employing a Dean−Stark trap for several days, only faint product spots were observed on TLC, with the overwhelming majority being unreacted starting material. This was surprising since other known semisquaraines lacking the *ortho*-amino group readily undergo such coupling reactions.[2]

The observed extraordinarily low reactivity of *ortho*-dialkylamino-substituted semisquaraines **7a**,**c** at both nucleophilic and electrophilic termini is probably due to an intramolecular hydrogen bonding interaction between the fairly acidic semisquaraine hydroxyl group and the aromatic *ortho*-nitrogen atom. Such interaction would lock the structure in a planar conformation, in which the squaryl ring in conjugation to the aromatic system acts as a strong acceptor and the *ortho*-amino group can no longer act as a donor since its lone pair is engaged in intramolecular hydrogen bonding. The net effect would

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(9) See Supporting Information for details.

(10) For a related procedure, see: Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477−2482.

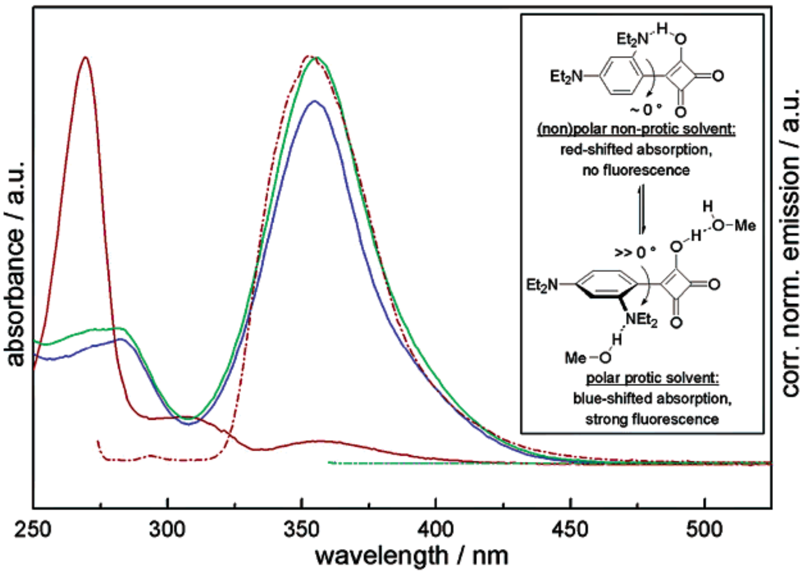

FIGURE 2. UV/vis absorption and fluorescence emission spectra of **7a** in CH_2Cl_2 (abs, solid blue line; emi, broken blue line), CH_3CN (abs, solid green line; emi, broken green line), and CH_3OH (abs, solide red line; emi, broken red line) ($\lambda_{exc} = 355$ nm for CH_2Cl_2 and CH_3CN and 269 nm for CH_3OH). The inset illustrates a simplified attempt to rationalize the dependence of photophysical properties on the protic/nonprotic medium.

be a shift of electron density from the phenylenediamine to the squaryl moiety via both conjugation and hydrogen-bonding pathways and hence a loss in nucleophilicity and electrophilicity, respectively. The UV/vis absorption and emission spectra of semisquaraine **7a** in different solvents provide experimental support for the existence of an intramolecular hydrogen bond. While the absorption spectra of **7a** displaying a maximum at $\lambda_{max} = 355$ nm are comparable for both extremes of nonpolar (methylene chloride) and polar nonprotic solvents (acetonitrile), polar protic solvents (methanol) cause a dramatic hypsochromic shift to $\lambda_{max} = 269$ nm (Figure 2). Furthermore, strong emission occurs only in methanol ($\lambda_{exc} = 269$ nm, $\lambda_{em} = 354$ nm). These results suggest the presence of an intramolecular N−H−O hydrogen bond in nonprotic media, while protic solvents destabilize the planar conformation and lead to the formation of a decoupled system with strongly altered electronic properties that are reflected in its drastically different photophysical behavior. Alternative techniques such as IR or ^{1}H NMR unfortunately failed to provide more direct evidence for an existing hydrogen bond; therefore, theoretical approaches were sought to gain more insight into the structure and electronic properties of semisquaraines **7**.

Computational Studies. To investigate the influence of a hydrogen-bonding interaction on the structural preferences of semisquaraines **7**, ab initio calculations using Gaussian 98[11] with the Hartree−Fock method and the 6-31G* basis set were carried out.[9] Starting from a fully optimized geometry, a rotamer series of **7a** was generated by fixing the C=C−O−H dihedral angle between 0 and 180°. Thereby, the hydrogen atom is moved from a planar hydrogen-bonded structure **7a-0** (0°) to orthogonal **7a-90** (90°) and finally planar **7a-180** (180°) non-hydrogen-bonded structures. Single-point energies as well as energies of the optimized geometries were calculated yielding the nonoptimized and optimized ground-state potential energy diagrams (Figure 3).[12]

The almost planar (phenyl-squaraine dihedral angle ~7°), hydrogen bonded structure **7a-0** is clearly the most stable conformation according to both initial computation and variation of the C=C−O−H dihedral angle. The stability of the planar structure arises from a strong intramolecular hydrogen bond as evidenced by comparison with the 18 kcal/mol less stable orthogonal conformation (nonoptimized). Geometry optimization for the given angle reduces the depth of the well ($\Delta\Delta G \approx 12$ kcal/mol), i.e., stabilizes the twisted conformations, mainly due to rehybridization of the *ortho*-nitrogen atom ($sp^3 \rightarrow sp^2$) and hence enhanced resonance energy. Further support for the key stabilizing hydrogen-bonding interaction arises from the existence of a second minimum on the potential energy surface that is approximately 6 kcal/mol less stable than **7a-0** and associated with the non-hydrogen-bonded structure **7a-180**, which shows significant deviation from planarity (phenyl−squaraine dihedral angle ≈ 36°). Natural bond order (NBO) analyses were performed to deduce charge distributions of the optimized rotamers. In particular, minimum hydrogen-bonded structure **7a-0** displays an increased natural charge on the *ortho*-nitrogen and a decrease in natural charge on the *meta*-carbon atom when compared to maximum orthogonal

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(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98,* revision A7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Diagram reflects only enthalpic contributions, i.e., differences in calculated heats of formation. However, entropic terms should be negligible when comparing (rotational) isomers.

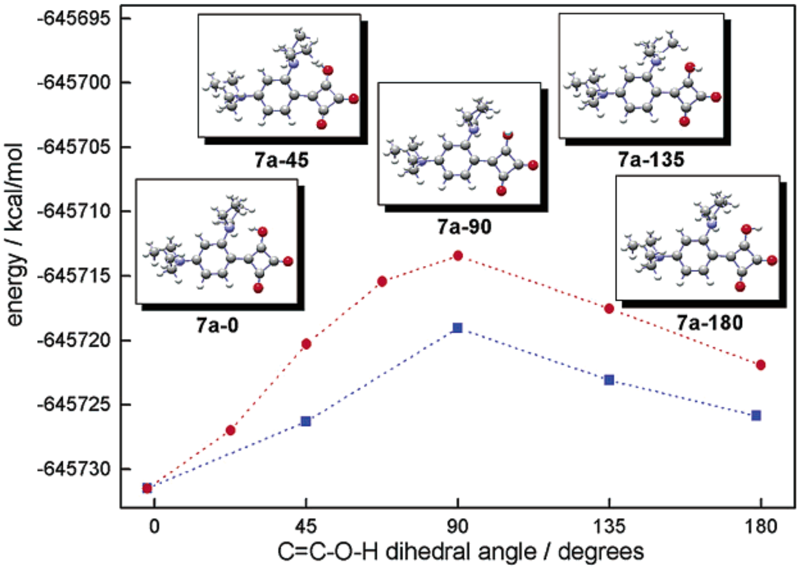

FIGURE 3. Potential energy diagram as a function of the C═C−O−H dihedral angle derived from ab initio calculations (Gaussian 98, HF, 6-31G*) on a preoptimized geometry of **7a**. Nonoptimized, single-point calculations (red circles) and fully optimized calculations for a given dihedral angle (blue squares) as well as selected respective fully optimized structures for 0° (**7a-0**), 45° (**7a-45**), 90° (**7a-90**), 135° (**7a-135**), and 180° (**7a-180**) are shown.

structure **7a-90**. Therefore, the computational results agree with the postulated effect of torsion on electron density distribution and therefore support the experimentally found unusual reactivity.

Conclusion

A novel class of *ortho*-dialkylamino-substituted semisquaraines has been synthesized and exhibits an intramolecular hydrogen bond that controls the conformational preference and hence the reactivity of the molecule. This finding, unfortunately, is the reason for our unsuccessful attempts to prepare poly(*m*-phenylene-*alt*-squaraine)s and is manifested in the fact that the semisquaraines themselves do not undergo an AB polycondensation reaction. The fact that alternative methods such as ketene dimerization followed by oxidation[13] also failed in our hands illustrates the need for conceptually new routes to assemble squaraine moieties and access the attractive family of poly(phenylene-*alt*-squaraine)s. Gratifyingly, the novel intramolecular hydrogen-bonding motif discovered during the course of our investigations displays a high sensitivity of photophysical properties on structural parameters and therefore offers potential applications in sensor design.

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Supporting Information Available: Experimental procedures, chemical characterization data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Farnum, D. G.; Webster, B.; Wolf, A. D. *Tetrahedron Lett.* **1968**, *8*, 5003−5006.