

Formation and Characterization of the Sulfur-Containing Distonic Radical Anion, $\text{CH}_2-\text{S}-\bar{\text{C}}\text{H}-\text{CN}$, in the Gas Phase

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The reactions of the atomic oxygen radical anion O^- with $\text{CH}_3-\text{S}-\text{CH}_2-\text{CN}$ in the gas phase have been examined with Fourier transform ion cyclotron resonance in combination with tandem mass spectrometric experiments performed with a double-focusing quadrupole hybrid instrument. Deuterium labeling has revealed that the O^- ion reacts with $\text{CH}_3-\text{S}-\text{CH}_2-\text{CN}$ by proton abstraction from the methylene group as well as by competing 1,1- and 1,3- H_2^+ abstractions to afford isomeric radical anions. High kinetic energy (8 keV) collision-induced charge reversal experiments indicate that the 1,1- H_2^+ -abstraction leads to a $\text{CH}_3-\text{S}-\bar{\text{C}}-\text{CN}$ carbene ion, whereas the 1,3- H_2^+ abstraction yields a novel sulfur-containing distonic radical anion, which is formulated as $\text{CH}_2-\text{S}-\bar{\text{C}}\text{H}-\text{CN}$. (*J Am Soc Mass Spectrom* 1995, 6, 71-75)

Distonic radical cations have been studied extensively and are well recognized as stable species and key intermediates in unimolecular as well as bimolecular reactions in the gas phase [1-5]. The interest in these ions arises in part from the finding that some simple distonic radical cations that contain a halogen, nitrogen, or oxygen atom (e.g., CH_2OH_2^+) are more stable than their conventional isomers (e.g., CH_3OH^+) [2, 6]. The opposite situation applies to simple sulfur-containing distonic radical cations [1, 7-13], which according to ab initio calculations are less stable than the conventional isomers [1, 7]. For example, the distonic radical cation $\text{CH}_2-\dot{\text{S}}\text{H}-\text{CH}_3$ is estimated to be about 80 kJ mol^{-1} higher in energy than the conventional $\text{CH}_3-\text{S}^+-\text{CH}_3$ ion [7]. In contrast to the extensive literature concerning distonic radical cations, very little is known about distonic radical anions. A few radical anions that may be classified as distonic have been generated. The reported examples include the $\text{CH}_2-\text{C}(\text{O}^-)=\text{CH}_2$ ion generated by a 1,3- H_2^+ abstraction in the reaction of O^- with acetone [14] and the CH_2CO_2^- ion formed in the reaction of the acetyl anion with molecular oxygen [15]. The latter ion has been reported to arise also by high kinetic energy collision-induced dissociation (CID)

of carboxylate anions derived from α,ω -dicarboxylic esters together with the homologous $\text{CH}_2(\text{CH}_2)_n\text{CO}_2^-$ ($n = 1$ and 2) species [16]. More recent examples include the $\text{C}_6\text{H}_4\text{CO}_2^-$ ion generated by addition of the orthobenzene radical anion to carbon dioxide [17], the $\text{C}_6\text{H}_3\text{F}^-$ ions formed by competing 1,4- and 1,3- H_2^+ abstractions in the reaction of O^- with fluorobenzene [18], and the radical anion of tetramethylene-ethane generated by a 1,4- H_2^+ abstraction from 2,3-dimethyl-1,3-butadiene [19]. In addition, a theoretical study of some simple metal-containing radical anions indicates that the classical isomers generally represent the preferred form of these species [20]. In particular, the isomers, $\text{H}_2\dot{\text{C}}-\text{LiH}^-$ and $\text{H}_2\dot{\text{C}}-\text{NaH}^-$, are predicted to be much higher in energy than the CH_3Li^- and CH_3Na^- species.

The reported examples of distonic radical anions suggest that the reactions of O^- with suitable organic substrates in the gas phase may provide a general and relatively facile method for the formation of these species. As part of our ongoing research into the formation and reactivity of various types of radical anions in the gas phase, we decided to explore whether distonic radical anions can be formed from simple molecules that contain a group capable of stabilizing a negative charge and a second functionality capable of stabilizing an adjacent radical center. Here we report our result for $\text{CH}_3\text{SCH}_2\text{CN}$, which was selected as a relatively simple and readily available model compound that fulfills these requirements.

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Experimental

The results were obtained in part with the use of a Fourier transform ion cyclotron resonance (FT-ICR) [21-23] mass spectrometer designed and constructed at the University of Amsterdam [24]. The experimental operating procedure of this instrument has been outlined elsewhere [25, 26]. The O^- ions were generated from N_2O by dissociative capture of electrons with an energy of 1.0-1.5 eV. The partial pressures of N_2O and thiomethylacetone were both $\approx 3 \times 10^{-5}$ Pa as measured with an uncalibrated ionization gauge placed in a side arm of the main pumping line. Unwanted ions were ejected from the FT-ICR cell by applying appropriate radiofrequency (rf) pulses to the excitation plates of the cell [27].

The CID and charge reversal (CR) spectra [28-30] were recorded with a Fisons ZAB-2HFqQ (Fisons Instruments, Manchester, UK) reverse geometry double-focusing quadrupole hybrid mass spectrometer [31, 32]. The CID experiments were carried out with He as the collision gas, whereas O_2 was used as the collision gas in the CR experiments. In both instances the gas was admitted to the collision cell located in the second field-free region until the intensity of the main beam of the mass-selected negative ions was reduced by 50%. The methylthioacetone sample was introduced into the combined electron impact (EI)-chemical ionization (CI) source with a direct insertion probe. The pressure of nitrous oxide was about 10^{-2} Pa as measured with an uncalibrated ionization gauge placed in a side arm of the entrance to the diffusion pump situated beneath the ion-source housing.

Materials

All samples were commercially available with the exception of the CH_3SCD_2CN ($\geq 95\%$ d_2) compound, which was prepared from the unlabeled compound by hydrogen-deuterium exchange in D_2O at room temperature. After removal of the water layer no further purification was needed. The identity of the compound, the label content, and the position of the deuterium atoms were confirmed by EI mass spectrometry.

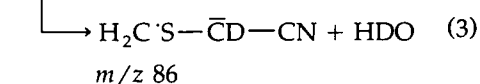
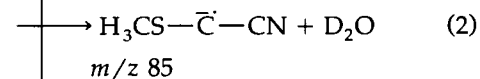
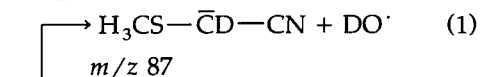
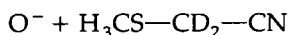
Results and Discussion

The O^- radical anion is known to react with a variety of organic compounds by abstraction of a hydrogen atom and a proton in an overall process, which is described commonly as a formal H_2^+ abstraction [33, 34]. In the reaction of O^- with methylthioacetone in the FT-ICR cell, competing proton transfer and H_2^+ abstraction occur. Deuterium labeling reveals that proton abstraction involves only the methylene position (eq 1), whereas two channels are open in the latter process; that is, competing 1,1- and 1,3- H_2^+ abstractions take place (eqs 2 and 3).

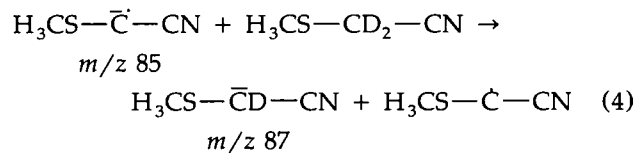
Table 1. Time dependence of the normalized abundances (%) of the ions formed in the reaction of the O^- ion with CH_3SCD_2CN in the gas phase as determined by Fourier transform ion cyclotron resonance^a

Time (ms)	$CH_3S-\bar{C}D-CN$	$CH_3-S-\bar{C}-CN$	$CH_2S-\bar{C}D-CN$
100	55	32	12
200	58	28	14
400	70	17	13
600	80	9	11
800	81	8	11
1000	85	4	11

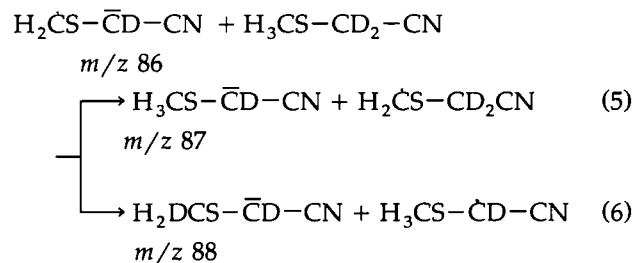
^a See text and eqs 4-6



In Table 1 the relative abundances of the different product ions are given as a function of reaction time. The radical anion formed by D_2^+ abstraction from the labeled compound reacts relatively readily with the parent compound to form the $CH_3-S-\bar{C}D-CN$ anion either by abstraction of a deuterium or a deuterium atom (eq 4).



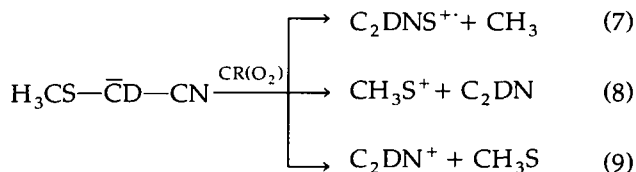
The radical anion generated by HD^+ abstraction reacts very slowly with the parent compound to afford the $CH_3-S-\bar{C}D-CN$ ion (eq 5) together with very minor amounts of an ion with m/z 88 (eq 6). The former ion can be generated either by deuterium abstraction or hydrogen atom transfer, whereas the m/z 88 ion may arise by deuterium atom abstraction from the parent compound.



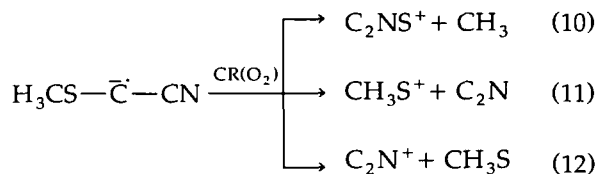
These FT-ICR experiments indicate that three different ions arise in the reaction of the O^- ion with methyl-

thioacetoneitrile. That is, proton abstraction leads to a carbanion, whereas two isomeric species are generated by the competing 1,1- and 1,3- H_2^+ abstractions. To structurally characterize these ions, high kinetic energy CID experiments were performed with a reverse geometry double-focusing instrument (see Experimental). The ion formed by deuteron abstraction eliminates only a methyl radical in the high kinetic energy collision experiments, in agreement with the proposed structure (see eq 1). The ion formed by D_2^+ abstraction expels also a methyl radical upon collision, as expected for the assumed structure (see eq 2). In contrast, no negatively charged product ions are formed in these experiments with the ion generated in the HD^+ abstraction, thus precluding a structural characterization of this ion by CID. However, the collision-induced CR spectra of the three ions proved to be distinct as can be seen in Figure 1.

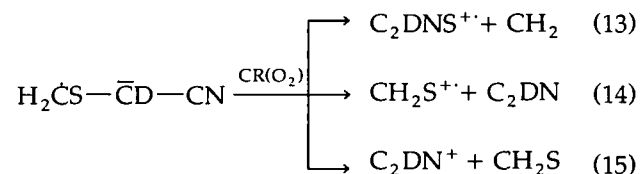
The CR spectrum of the carbanion (Figure 1a) displays a peak that corresponds to C_2DNS^+ ions generated by the expulsion of a CH_3 radical (eq 7) together with peaks for the formation of CH_3S^+ and C_2DN^+ ions (eqs 7-9).



In the CR spectrum of the supposed carbene radical anion, peaks that correspond to CH_3S^+ and C_2N^+ ions are noticed (Figure 1b) together with a peak of an ion formed by methyl radical loss (eqs 10-12).



Significantly, the CR spectrum of the radical anion (Figure 1c) generated by HD^+ abstraction contains a peak that corresponds to an ion formed by the expulsion of a CH_2 fragment as well as signals for CH_2S^+ and C_2DN^+ ions (eqs 13-15).



The CR spectra support the structural assignments of the carbanion and the carbene radical anion. For the ion generated by HD^+ abstraction, the expulsion of CH_2 and the absence of a peak corresponding to

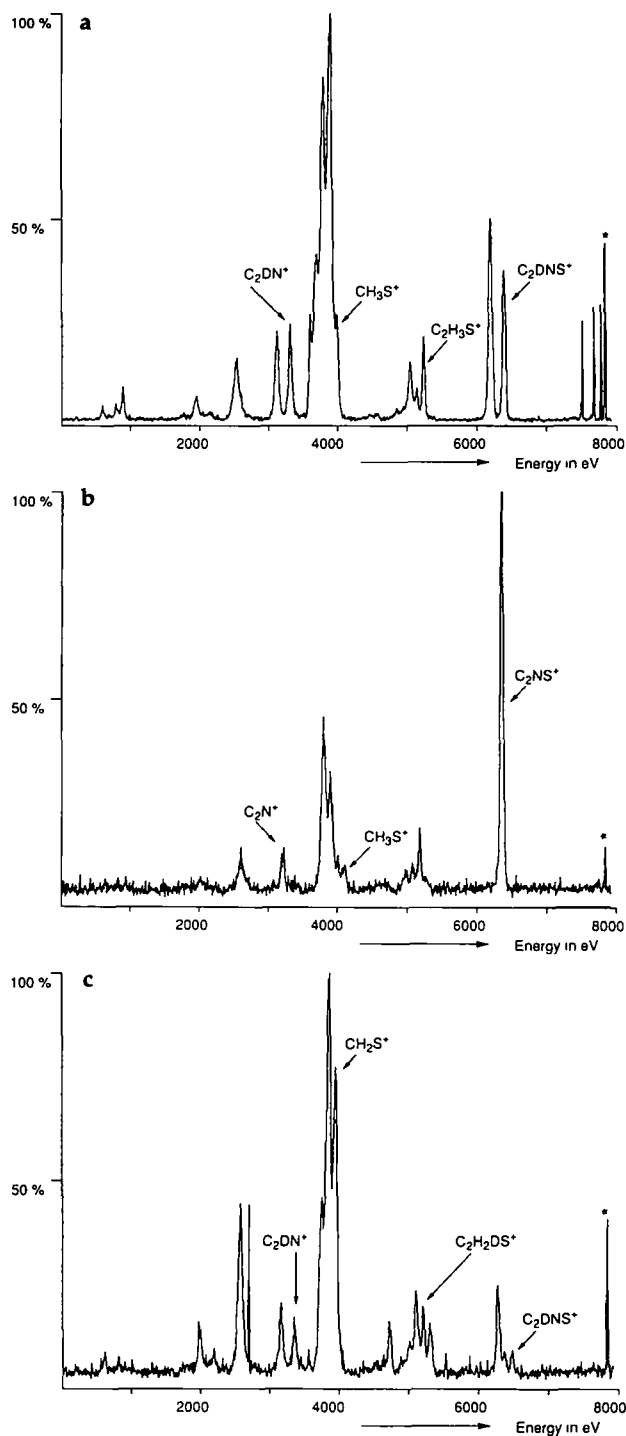


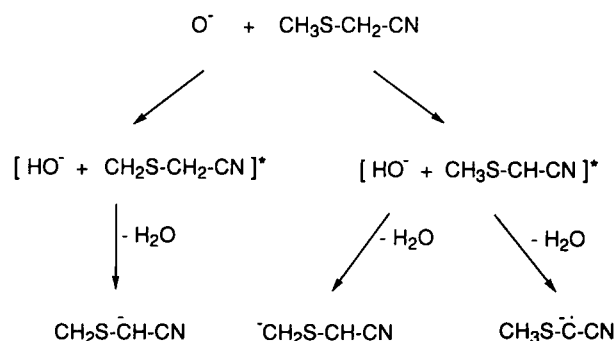
Figure 1. Collision-induced charge-reversal spectra of the ions formed in the reactions of the O^- ion with methylthio-2,2- d_2 -acetoneitrile in a chemical ionization source (a) $\text{CH}_3-\text{S}-\bar{\text{C}}\text{D}-\text{CN}$, (b) $\text{CH}_3-\text{S}-\bar{\text{C}}-\text{CN}$, and (c) $\text{CH}_2-\text{S}-\bar{\text{C}}\text{D}-\text{CN}$; see also text. The peaks marked with an asterisk correspond to the charge-reversed and mass-selected parent ion. A few spikes are present as very narrow signals in spectra (a) and (c)

CH_3S^+ (Figure 1c) strongly suggest that a distonic sulfur-containing radical anion is generated.

Based on the present results it is not possible to ascertain the location of the charge and radical site

within the distonic ion. In the equations, we have located the negative charge in a formal sense on the carbon atom in between the sulfur atom and the CN function and the radical position on the carbon atom bonded only to the sulfur atom. This is based largely on the observation that CH_3SCH_3 is about 85 kJ mol^{-1} less acidic [35] than acetonitrile [36] in the gas phase, which indicates that the cyano group stabilizes a negative charge on an adjacent carbon atom better than a $-\text{SCH}_3$ group. The distonic ion may, of course, also be formulated as $^-\text{CH}_2-\text{S}-\dot{\text{C}}\text{HCN}$. Only few homolytic C—H bond dissociation energies (BDE) of simple sulfur-containing compounds have been reported. It may be noted, however, that the homolytic C—H BDE of CH_3SH ($\approx 387 \text{ kJ mol}^{-1}$) [37, 38] is close to the value for CH_3CN ($\approx 390 \text{ kJ mol}^{-1}$) [37, 39]. This suggests that the stabilization of the radical site will not differ drastically if located on the central carbon atom or on the carbon atom bonded only to the sulfur atom. In other words, the stabilization of the radical site may not be the crucial factor in determining the radical/charge distribution in the distonic ion.

The formation of the distonic radical anion can involve initial hydrogen atom abstraction followed by proton abstraction as proposed also for the formation of the orthobenzynes radical anion in the reaction of O^- with benzene [17, 40]. If the hydrogen atom abstraction occurs from the methyl group, proton abstraction from the methylene function can follow and lead to the $^-\text{CH}_2\text{S}-\dot{\text{C}}\text{H}-\text{CN}$ species (Scheme I). Hydrogen atom abstraction may also occur from the methylene group and be followed either by proton abstraction from this site with formation of the carbene radical anion or from the methyl group. In the latter instance, proton abstraction generates the distonic radical anion with the charge on the carbon atom bonded only to the sulfur atom (see Scheme 1). Nevertheless, electronic reorganization may occur and lead to the anticipated formal location of the negative charge in between the functional groups. Further work on the stability and reactivity of the sulfur-containing distonic radical anion in comparison to isomeric ions is in progress.



Scheme I. Possible pathways that lead to formation of the distonic radical anion (see also text)

Acknowledgments

The authors thank the Netherlands Organization for Scientific Research (SON/NWO) for financial support. The authors acknowledge H. E. K. Matimba for his assistance during the experiments with the double-focusing reverse geometry hybrid instrument.

References

1. Yates, B. F.; Bouma, W. J.; Radom, L. *J Am. Chem. Soc.* **1984**, *106*, 5805-5808.
2. Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831-1842.
3. Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123-202.
4. Bjørnholm, T.; Hammerum, S.; Kuck, D. *J Am. Chem. Soc.* **1988**, *110*, 3862-3869.
5. Strk, K. M.; Kimunkinen, L. K. M.; Kenttamaa, H. I. *Chem. Rev.* **1992**, *92*, 1649-1665.
6. Bouma, W. J.; MacLeod, J. K.; Radom, L. *J Am. Chem. Soc.* **1982**, *104*, 2930-2931.
7. Nobes, R. H.; Bouma, W. J.; Radom, L. *J Am. Chem. Soc.* **1984**, *106*, 2774-2781.
8. Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Can J Chem.* **1983**, *61*, 2305-2309.
9. van Amsterdam, M. W.; Zappey, H. W.; Ingemann, S.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1993**, *28*, 30-36.
10. van Amsterdam, M. W.; Staneke, P. O.; Ingemann, S.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1993**, *28*, 919-920.
11. Nibbering, N. M. M.; Ingemann, S.; de Koning, L. J. *The Chemistry of Sulfur-Containing Functional Groups*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1993, pp 293-337.
12. Strk, K. M.; Orłowski, J. C.; Leeck, D. T.; Kenttamaa, H. I. *J Am. Chem. Soc.* **1992**, *114*, 8604-8606.
13. Smith, R. L.; Chyall, L. J.; Strk, K. M.; Kenttamaa, H. I. *Org. Mass Spectrom.* **1993**, *28*, 1623-1631.
14. Dawson, J. H. J.; Noest, A. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 189-191.
15. DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J Am. Chem. Soc.* **1985**, *107*, 3385-3386.
16. Maas, W. P. M.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *88*, 257-266.
17. Guo, Y.; Grawbowski, J. J. *J Am. Chem. Soc.* **1991**, *113*, 5923-5931.
18. Matimba, H. E. K.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 73-81.
19. Lee, J.; Chou, P. K.; Dowd, P.; Grabowski, J. J. *J Am. Chem. Soc.* **1993**, *115*, 7902-7903.
20. Pius, K.; Chandrasekhar, J. *J. Chem. Soc. Perkin. Trans. 2* **1988**, 1291-1295.
21. Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489-490.
22. Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282-283.
23. Marshall, A. G.; Verdun, R. F. *Fourier Transforms in NMR, Optical and Mass Spectrometry*, Elsevier Amsterdam, 1990.
24. Nibbering, N. M. M. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 747-748.
25. de Koning, L. J.; Kort, C. W. F.; Pinkse, F. A.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *95*, 71-92 and references cited therein.
26. Peerboom, R. A. L.; Ingemann, S.; Nibbering, N. M. M.; Liebman, J. F. *J. Chem. Soc. Perkin Trans. 2* **1990**, 1825-1828 and references cited therein.
27. Heck, A. J. R.; de Koning, L. J.; Pinkse, F. A.; Nibbering, N. M. M. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 406-414.
28. Bursley, M. M. *Mass Spectrom. Rev.* **1990**, *9*, 555-574.

29. de Lange, W.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1985**, *107*, 111-125.
30. Szulejko, J. E.; Bowie, J. H.; Howe, I.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99-111.
31. Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 171-191.
32. Harrison, A. G.; Mercer, R. S.; Reiner, E. J.; Young, A. B., Boyd, R. K.; March, R. E., Porter, C. J. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 13-31.
33. Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611-1647
34. Nibbering, N. M. M. *Adv. Phys. Org. Chem.* **1988**, *24*, 1-55.
35. Ingemann, S., Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273-2281.
36. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Chem. Phys. Ref. Data* **1988**, *17*, suppl. 1.
37. Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744-2765.
38. Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc. Chem. Commun.* **1984**, 731-732.
39. Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *Chem. Phys. Lett.* **1993**, *212*, 134-140.
40. Matimba, H. E. K., Crabbendam, A. M., Ingemann, S.; Nibbering, N. M. M. *J. Chem. Soc. Chem. Commun.* **1991**, 644-645.