We suggest that the ground-state distortion of MCl_4^- is eliminated in the excited state. The stabilization of the C_{2v} butterfly structure is essentially lost in the $a'_1{}^* \rightarrow b'_1{}^*$, $a'_1{}^*$, $b'_2{}^*$ sp excited state (Figure 3) which rearranges toward a symmetrical tetrahedral geometry. This structural change now explains easily the immense Stokes shift of MCl_4^-.

An analogous approach has been used before in solid-state physics. Blasse and his group have shown that s^2 ions which are doped into host lattices may also show large Stokes shifts if the ions occupy off-center positions in large interstices since these s^2 ions can move toward the center in the sp excited state.[3]

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Professor G. Blasse for helpful discussions.

Registry No. $SbCl_4^-$, 18443-80-6; $SbCl_6^{3-}$, 16283-39-9; $BiCl_4^-$, 20057-70-9; $BiCl_6^{3-}$, 15977-99-8.

The Return of the Trapped Electron in X-Irradiated Clathrate Hydrates. An ESR Investigation

Janusz Bednarek,[§,†] Roland Erickson,[‡] Anders Lund,[‡] and Shulamith Schlick*[,§]

Department of Chemistry, University of Detroit
Detroit, Michigan 48221
Department of Physics, Linkoping University
S-5 81 83 Linkoping, Sweden

Received April 24, 1991

The search of an ideal host for the formation and detection of trapped electrons in organic single crystals has lead us to a large family of clathrate hydrates containing peralkylammonium hydroxide guests. The presence of trapped electrons has been detected by pulse radiolysis at room temperature in a large number of the clathrates.[1,2]

Two compounds were chosen for this initial study of electron stabilization: tetramethylammonium hydroxide pentahydrate, $(CH_3)_4N^+OH^-\cdot 5H_2O$, mp 335 K (TMNOH, I), and tetra-*n*-butylammonium hydroxide hydrate, $(C_4H_9)_4N^+OH^-\cdot 31H_2O$, mp 303 K (TBNOH, II). This selection was made because the crystal structure for both hydrates has been determined,[3,4] the melting points are above ambient temperature, and because the amount of water in the stoichiometric compounds is large, about 50% by weight in I and 68% in II; therefore, the radiolytic behavior of these hydrates can be compared to the well-known results for other forms of water (ice, liquid, and glass).

Compound II has the typical crystal structure of most peralkylammonium hydrates based on the pentagonal dodecahedral unit. Compound I is unique among the peralkylammonium hydrates, in that its structure is based on a truncated octahedron and is shown in Figure 1.[4,5] The distances between the nitrogen (N) in the center and the oxygen atoms of the cage range from 4.30 (to O1) to 4.97 Å (to O2), and the average is 4.61 ± 0.16 Å.

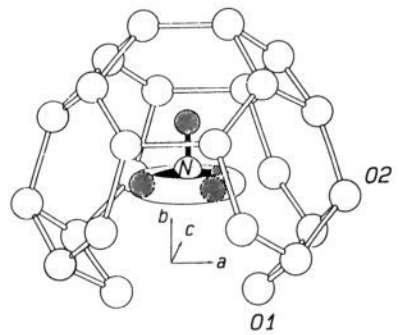


Figure 1. A distorted truncated octahedron containing the $(CH_3)_4N^+$ ion in the tetramethylammonium hydroxide clathrate. The three disordered CH_3 groups are represented by the torus and the hydrogen atoms are omitted (redrawn from ref 4).

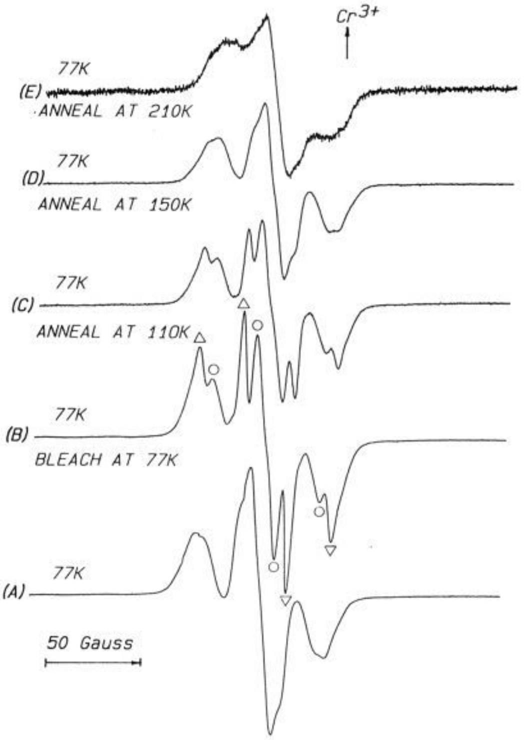


Figure 2. X-band ESR spectra at 77 K of X-irradiated TMNOH clathrate hydrate: (A) immediately after irradiation, (B) after optical bleaching, and (C)–(E), after 3 min annealing at the indicated temperatures. In (B) the signals assigned to the methyl and $N\text{–}CH_2^{\bullet}$ radicals are shown by (△) and (○), respectively.

Exciting results have been reported recently on some clathrates, using ^{129}Xe NMR[6] and gas-phase mass spectroscopic techniques.[7] The renewed interest in the clathrate hydrates is expected to increase our understanding of this ubiquitous class of compounds.

Crystalline TMNOH and TBNOH were purchased from Fluka. X-irradiations were done for 30–60 min at 77 K in the dark. All ESR measurements were done at 77 K with a Bruker 200D spectrometer operating at 9.7 GHz with 100 kHz modulation, using a low microwave power to prevent saturation of the signal from trapped electrons. Optical bleaching of the irradiated samples was accomplished with a slide projector.

Both TMNOH and TBNOH became intensely blue after X-irradiation in the dark, indicating the presence of trapped electrons. The blue color disappears by optical bleaching.

X-band ESR spectra of irradiated TMNOH clathrate at 77 K are given in Figure 2A–E. Bleaching of the central part of the spectrum is accompanied by resolution enhancement of the remaining signals, as seen in Figure 2B. The spectrum in Figure

---

[*] Author to whom correspondence should be addressed.

[†] On leave from the Institute of Applied Radiation Chemistry, Technical University, Lodz, Poland.

[§] University of Detroit.

[‡] Linkoping University.

(1) (a) Zagorski, Z. P. *Nucleonika* **1981**, *26*, 869. (b) Zagorski, Z. P. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1989**, *7*, 569.

(2) (a) Zagorski, Z. P. *Chem. Phys. Lett.* **1985**, *115*, 507. (b) Zagorski, Z. P. *J. Phys. Chem.* **1987**, *91*, 734. (c) Zagorski, Z. P. *J. Phys. Chem.* **1987**, *91*, 972.

(3) McMullan, R.; Jeffrey, G. A. *J. Chem. Phys.* **1959**, *31*, 1231.

(4) McMullan, R.; Mak, T. C. W.; Jeffrey, G. A. *J. Chem. Phys.* **1966**, *44*, 2338.

(5) Jeffrey, G. A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D. Eds.; Academic Press: New York, 1984; Vol. 1, p 135.

(6) Ripmeester, J. A.; Ratcliffe, C. I. *J. Phys. Chem.* **1990**, *94*, 8773.

(7) (a) Yang, X.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6845. (b) Yang, X.; Castleman, A. W., Jr. *J. Phys. Chem.* **1990**, *94*, 8500. (c) Wei, S.; Shi, Z.; Castleman, A. W., Jr. *J. Chem. Phys.* **1991**, *94*, 3268.

0002-7863/91/1513-8990$02.50/0 © 1991 American Chemical Society

2B appears to consist of two radical species. A quartet with a proton splitting of 23 G (triangles in Figure 2) suggests the presence of the methyl radical; a triplet with two almost equivalent protons and a splitting of 24 G (circles) suggests the fragment $N-CH_2^\bullet$. The lines from the triplet are broader than for the quartet, suggesting an additional small splitting of <5 G, possibly from the ^{14}N nucleus. Both spectra are centered at $g = 2.0022$, as expected for organic radicals. An approximate ESR spectrum from the trapped electron, obtained by subtracting 2B from 2A, has a peak-to-peak line width of $\approx$12 G and is centered at $g = 2.0008$.

After bleaching the sample was annealed for 3 min at a given temperature, followed by measurement at 77 K, as shown in Figure 2C–E. The most dramatic change is seen in Figure 2D: After annealing at 150 K, the original spectrum given in Figure 2A is recovered and includes the bleachable central signal assigned to the trapped electron. The reappearance of this signal is accompanied by a blue coloration of the sample, thus providing additional proof for *the return of the trapped electron.* Further annealing leads to decay of all signals; above 220 K no signals are detected. The main features observed for the TMNOH hydrate clathrate are also detected for X-irradiated TBNOH.[8] In both hydrates the improved resolution of the spectra after optical bleaching suggests that the trapped electron and the alkyl radicals interact by magnetic dipole–dipole interaction, which causes line broadening. It is possible that the alkyl radicals *and* the electrons are trapped in the same cavity and are the result of the same radiolytic event. This conclusion is logical, in view of the crystal structure given in Figure 1: The cage diameter is about 9.2 Å, large enough to accommodate the electron and an alkyl radical.

The great stability of the trapped electrons, to about 200 K, and the return of the signal from trapped electrons after optical bleaching and annealing to $\approx$150 K are the most significant observations deduced in the present study. It is likely that the unusual stability of the electrons is due to their trapping in the vicinity of the peralkylammonium cation, which has a high reduction potential and is therefore a poor electron scavenger.[1a]

Symons et al. proposed a mechanism for the reappearance of the electrons: The electrons disappear on photobleaching due to reaction with O^- to produce OH^- and reappear by reaction of H atoms with OH^-.[9] Because we have not detected either O^- or its acid form the OH radical in our system, we must seek an alternative explanation for the reappearance of the electrons. We propose that the diamagnetic species formed by optical bleaching is the electron pair e_{2t}^{2-}, which dissociates around $\approx$150 K and releases the trapped electron.

The existence of trapped electron pairs is well-documented experimentally and theoretically in ionic crystals;[10] in irradiated 6 M NaOH glasses, the disappearance of the signal from trapped electrons for a high irradiation dose was explained by the formation of the dielectron.[11-13] Evidence for the trapping of electron pairs has also been obtained in a polycrystalline K^+ (cryptand[2.2.2]) electride.[14,15] The vacancy size in the cryptand is $\approx$300 Å^3, similar to the cage size in the TMNOH hydrate, which is $\approx$400 Å^3. The cavity size appears to be important for the stability and reactivity of the electrons and of the electron pairs.

To the best of our knowledge we have reported here the first evidence for trapped electron pairs in polycrystalline hydrate clathrates. Further studies are in progress, in order to characterize in greater detail the electron site, the interaction between the radicals produced by irradiation, the stability of the electron pairs, and the conductivity at low temperatures.

Acknowledgment. This study was supported by NSF Grants INT-8610708 (Cooperative Research US-Sweden) and DMR-8718947 (Polymer Program) and by the Swedish Science Research Council. We are grateful to Larry Kevan for illuminating discussions on the trapped dielectron.

---

(8) Bednarek, J.; Erickson, R.; Lund, A.; Schlick, S., to be published.

(9) Symons, M. C. R.; Zimmermann, D. N. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 395.

(10) Fowler, W. B. *Physics of Color Centers*; Academic Press: New York, 1968.

(11) Zimbrick, J.; Kevan, L. *J. Am. Chem. Soc.* **1967**, *89*, 2483.

(12) Kevan, L.; Renneke, D. R.; Friauf, R. J. *Solid State Commun.* **1968**, *6*, 469.

(13) Feng, D. F.; Fueki, K.; Kevan, L. *J. Chem. Phys.* **1973**, *58*, 3281.

(14) Huang, R. H.; Faber, M. K.; Moeggenborg, K. J.; Ward, D. L.; Dye, J. L. *Nature* **1988**, *331*, 599.

(15) Edwards, P. P. *Nature* **1988**, *331*, 564.

---

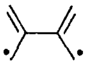
p-Phenylene-2,2′-bis(1,1:3,3-di-2,2′-biphenylenepropenyl): A Stable Non-Kekule Molecule as a Ground-State Singlet

Hideyuki Tukada

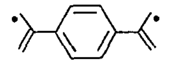
Department of Chemistry
College of Arts and Sciences
The University of Tokyo, Komaba
Tokyo 153, Japan

Received July 22, 1991

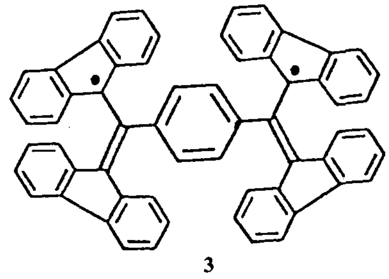
One of the interests in non-Kekule molecules[1] is to elucidate a relation between topological property of π-conjugation and ground-state spin multiplicity. For example, tetramethyleneethane (TME, **1**) is predicted to be a singlet ground state according to a classical formalism of $S = (n^*-n^0)/2$.[2] Ab initio calculations also confirm that the singlet state of **1** is slightly below the triplet state at any conformation about the central allyl–allyl bond.[3] However, conflict between theory and experiment is claimed by Dowd that the triplet is the ground state of both **1** and 2,3-dimethylenecyclohexa-1,3-diene based on ESR experiments.[4,5]



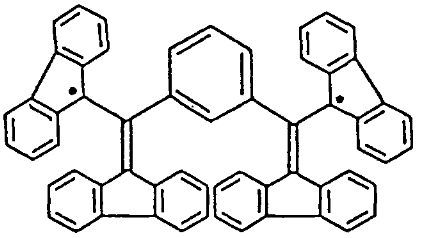
1



2



3



4

---

(1) For example: (a) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (b) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4, pp 151. (c) Platz, M. S. In *Diradicals*; Chapter 5, p 195. (d) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88. (e) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron*, **1982**, *38*, 787. (f) Michl, J.; Bonacic-Koutecky, V. *Tetrahedron* **1988**, *44*, 7559. (g) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030.

(2) (a) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (b) Lieb, E. H.; Mattis, D. C. *J. Math. Phys.* **1962**, *3*, 749.

(3) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930.

(4) (a) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416; **1987**, *109*, 5284. (b) Neugebauer, F. A.; Fischer, H.; Meier, P. *Chem. Ber.* **1980**, *113*, 2049.

(5) Several experimental results were reported on diradicals isomorphic to TME. (a) *m*-Phenylenebis(phenylmethylene) (singlet ground state, $\Delta E_{(S-T)} = 45$ cm^{-1}): Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251. (b) 2,3,5,6-Tetramethylene-1,4-cyclohexanediyl (triplet ground state): Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Muller. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256. (c) 2,6-Dimethyleneanthracenediyl-4,8-dioxy (triplet ground state): Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146.

0002-7863/91/1513-8991$02.50/0 © 1991 American Chemical Society