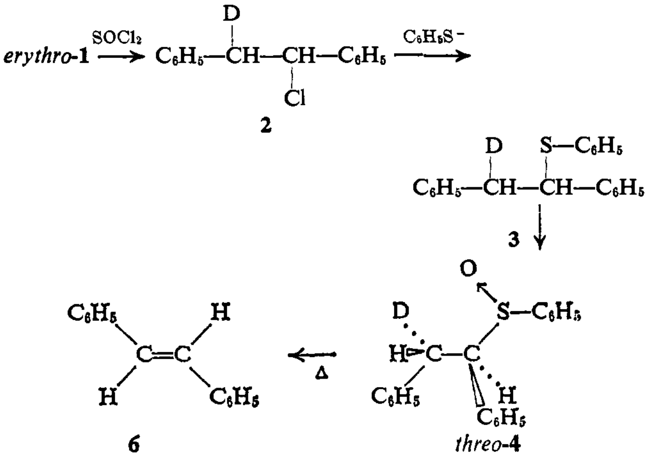
Scheme I



(*c* 5, EtOH), was converted into **2**, $[\alpha]^{25}\text{D}$ +9.30° (*c* 10.5, EtOH), as before.

In a second series of experiments, a reaction involving predominant racemization was investigated. *erythro*-**1** was treated with concentrated HCl with added LiCl to yield **2**. This product was converted into **3** in 85% yield. The phenyl sulfide **3** was 44% *erythro* and 56% *threo* isomers. Beginning with *threo*-**1**, product **3** again showed the product ratios 52% *erythro* and 48% *threo*, corresponding to near 100% optical racemization. Optically active **1**, $[\alpha]^{25}\text{D}$ +46.88° (*c* 5, EtOH), was treated with LiCl–HCl forming **2**, $[\alpha]^{25}\text{D}$ −0.34 (*c* 13.45, EtOH).

Figure 2 shows the partial nmr spectra of **3** prepared in stereospecific and nonstereospecific manners.

This study demonstrates the relative merits of the nmr method as opposed to the optical rotation method.

The optical rotation method is probably more accurate and will remain the method of choice where oxygen nucleophiles are to be used.

The one great advantage of the nmr method is that the amount of retention product and of inversion product can be *directly observed* in most cases, and it may find application in displacements where oxygen nucleophiles are not used.

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Structure of a Silver–Bullvalene Complex[1]

Sir:

Stimulated by the prediction of the unusual properties to be expected of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene or bullvalene (I),[2] and its subsequent synthesis,[3] considerable interest has been exhibited in the behavior and geometry of this extreme example of a "fluctional structure."[4–6] Allerhand and Gutowsky[6] prepared some Ag$^+$–bullvalene complexes in which the rate of self-rearrangement of bullvalene was reduced, and in the course of their work they isolated some solid complexes. Preliminary X-ray studies[7] on some of these compounds indicated that they possessed a very low degree of crystallinity which might be a result of crystallographic disorder among the bullvalene tautomers. We now report the results of a single crystal structure analysis of a new AgBF$_4$–bullvalene (1:3) complex, prepared by recrystallization of the previously reported 1:2 complex,[6] which had been standing for several weeks and had apparently partially decomposed, leaving an unidentified deposit.

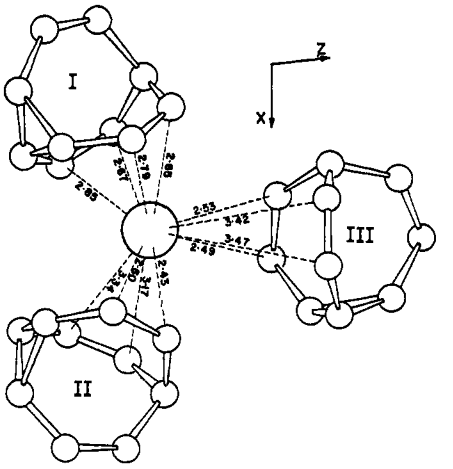

Figure 1. Perspective drawing of the Ag$^+$(bullvalene)$_3$ portion of the molecule viewed down the *b* axis. The important Ag$^+$–C (olefin) distances are shown in angstrom units.

I

This $(C_{10}H_{10})_3\cdot AgBF_4$ complex[8] crystallizes as white needles which darken on prolonged exposure to light. They belong to the monoclinic system with a = 12.44 ± 0.02, b = 10.18 ± 0.02, c = 19.47 ± 0.03 A, and β = 95° 40′ ± 10′, as determined on a precession camera using Mo Kα radiation (λ 0.7107 A). The space group is P2$_1$/c with four molecules of $(C_{10}H_{10})_3\cdot AgBF_4$ in the unit cell.[9] A total of 1734 independent structure amplitudes was obtained from visual estimates of equiinclination Weissenberg photographs (Cu Kα, λ 1.5418 A) taken at 4°.[10]

The crystal structure was solved by the heavy-atom method,[11] and a perspective view of the atomic arrangement looking down the *b* axis is shown in Figure 1. At the present stage of refinement the crystallographic *R* factor is 0.12.[12]

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[1] This work was supported in part by the National Institutes of Health (GM 12470-02 and 5T1 GM 722-05).

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[3] G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963).

[4] W. von E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).

[5] M. Saunders, *Tetrahedron Letters*, 1699 (1963).

[6] A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).

[7] I. C. Paul, unpublished work.

[8] Analytical data: Calcd: C, 61.5; H, 5.13. Found: C, 61.3; H, 5.25.

[9] We had only a few well-formed crystals, and virtually all of those were used in characterization and data collection. We have been unable to get a reliable estimate of the density from those remaining, as the complex readily dissolves in most organic solvents and all our measured values have been much higher than the calculated density of 1.59 g/cm^3.

[10] The data were collected in a cold room as under these conditions no observable intensity changes were detected over a period of 4–5 days. Three crystals were required to accumulate the data used in this analysis.

[11] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

[12] The fluoroborate anion appears to be partially disordered, as has been found in other structures,[13,14] but as this ion has approximately the same *x* and *z* coordinates as the Ag$^+$ ion, the details of this area of the unit cell may be subject to distortion owing to diffraction effects.

[13] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 477 (1965).

[14] I. C. Zimmermann, M. Barlow, and J. D. McCullough, *Acta Cryst.*, **16**, 883 (1963).

The three bullvalene molecules are orientated around the central Ag^+ ion and occupy positions about a pseudo-threefold symmetry axis through the Ag^+ ion (Figure 1). There are twelve possible bonding Ag^+–C (olefin) distances ranging from 2.43 to 3.47 A. The mode of complexation of Ag^+ to the olefinic double bonds differs among the three bullvalene molecules. In the case of molecules II and III (Figure 1), the interaction appears to be quite localized to one double bond resulting in a mean Ag^+–C distance of 2.51 A and a very much weaker interaction with one of the other double bonds resulting in a mean Ag^+–C contact of 3.35 A. In molecule I, however, complex formation involves two of the olefin bonds to an almost equal extent, corresponding to four Ag^+–C distances in the range 2.65–2.85 A. This structure represents the highest Ag^+–olefin coordination which has been studied crystallographically and indicates that a wide range of Ag^+–C (olefin) contacts are permissible, when steric and packing factors favor complexation.

There is no evidence for the presence of other tautomeric forms of bullvalene occupying the same crystallographic positions in some of the unit cells. In this complex it therefore appears that the rapid self-rearrangement of bullvalene has been effectively "frozen" in the solid state.

A more detailed discussion of the bonding and the full crystallographic results will be published at a later date.

Acknowledgment. We wish to thank Professor H. S. Gutowsky for bringing the problem to our attention and for his continued interest in the work. Dr. Adam Allerhand kindly provided us with samples of the solid complexes which he had prepared, and Mr. James McKechnie assisted at several stages of the analysis.

(15) Author to whom inquiries concerning this communication should be addressed.

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The Photoexcited Triplet State of the Azulenium Cation[1]

Sir:

A number of attempts have been made to detect the lowest triplet state, T_1, of the odd-alternant aromatic hydrocarbon azulene by studying its emission properties in rigid glasses.[2] Thus far no direct evidence has been reported for this state by optical methods although indirect evidence from studies of the quenching of anthracene[2b] and naphthacene[3] triplets indicates that it probably lies between 31 and 39 kcal/mole above the ground state.[3] The difficulty in detecting the lowest triplet state arises because of a combination of short radiative and radiationless lifetimes for the first and second excited singlet states and a fast radiationless $T_1 \rightarrow S_0$ process.[4] These difficulties can be overcome in certain cases by using heavy atom solvents such as krypton or xenon to increase the rate of triplet population[4] or by forming a suitable charge-transfer complex in which the first excited charge-transfer state lies above the lowest triplet state of azulene.[5] The triplet population can be enhanced in the latter case by intersystem crossing between the excited charge-transfer state and the triplet state of azulene. However, attempts to observe such an enhancement for several different charge-transfer complexes of azulene (TCNQ, iodine, trinitrobenzene) by epr techniques were unsuccessful.[6] An alternative possibility, involving the formation of the azulenium ion (which can be considered as a strong σ-type complex), was therefore investigated, and the results are reported in this communication.

The azulenium cation was formed by dissolving small amounts of azulene in freshly distilled trifluoroacetic acid at room temperature (final concentration *ca.* 10^{-2} *M*). Under these conditions the azulene is presumed to be monoprotonated; this was confirmed by observation of the nmr spectrum which showed the pattern expected for the azulenium ion protonated in the 1 position.[7] Upon slow cooling to liquid nitrogen temperatures the solution formed a rigid glass without any visible change in color (pale yellow-brown). The glass was irradiated at low temperatures with a 1000-w PEK Hg lamp. Suitable Corning Glass filters were used to exclude all light outside the wavelength region of the first absorption band (~320 to 370 mμ) of the cation.[8]

The epr spectrum, observed under conditions of continuous illumination, consisted of a broad anisotropic signal (line width 35 gauss; signal-to-noise ratio *ca.* 30:1) at 1592 ± 5 gauss corresponding to the $\Delta m = 2$ transition of the azulenium triplet, and a much stronger signal at 3325 ± 2 gauss due to the radicals formed during the irradiation.[9] No signals corresponding to $\Delta m = 1$ transitions for the triplet were observed for the azulenium ion.[10] The $\Delta m = 2$ signal disappeared with a decay constant of 1.2 ± 0.1 sec when the light was switched off, while the radical signal persisted for a period of several hours. The intensity of the $\Delta m = 2$ signal follows the expected Curie law behavior over the temperature range 90–143°K; above 145°K the signal was not detectable above the spectrometer noise.

A detailed description of the mechanism of triplet formation in the azulenium ion requires further optical studies. However, since the only light effective in producing triplets is that with a wavelength of *ca.* 350 mμ, the simplest mechanism is one in which the cation is excited to the lowest excited singlet state S_1 and then crosses over into a low-lying triplet T_1.[11]

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[1] Work supported by the U. S. Atomic Energy Commission.

[2] (a) G. Visivanath and M. Kasha, *J. Chem. Phys.*, **24**, 574 (1956); (b) W. R. Ware, *ibid.*, 37, 923 (1963).

[3] A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, **42**, 1715 (1965).

[4] G. W. Robinson and R. P. Frosch, *ibid.*, **38**, 1187 (1963).

[5] S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

[6] D. J. Blears and S. S. Danyluk, unpublished observations.

[7] S. S. Danyluk and W. G. Schneider, *Can. J. Chem.*, 40, 1777 (1962).

[8] E. Heilbronner, "Non-Benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V, p 256.

[9] No triplet signal was observed for azulene in diethyl ether or EPA glasses under similar conditions. However, Smaller (private communication) has detected a weak $\Delta m = 2$ signal for azulene in EPA at 77°K using a spectrometer with somewhat better sensitivity. In view of the short lifetimes predicted for the triplet state[4] it is possible that the weak signal is due to small amounts of naphthalene impurity.

[10] Weak $\Delta m = 1$ transitions were observed in the spectrum for the photoexcited triplet of the 1:1 azulene–boron trifluoride complex. However, it is not clear whether these are due to a triplet of the complex or to the presence of azulenium ions formed by reaction with trace amounts of H_2O–BF_3.

[11] The existence of a low-lying triplet is further indicated by the