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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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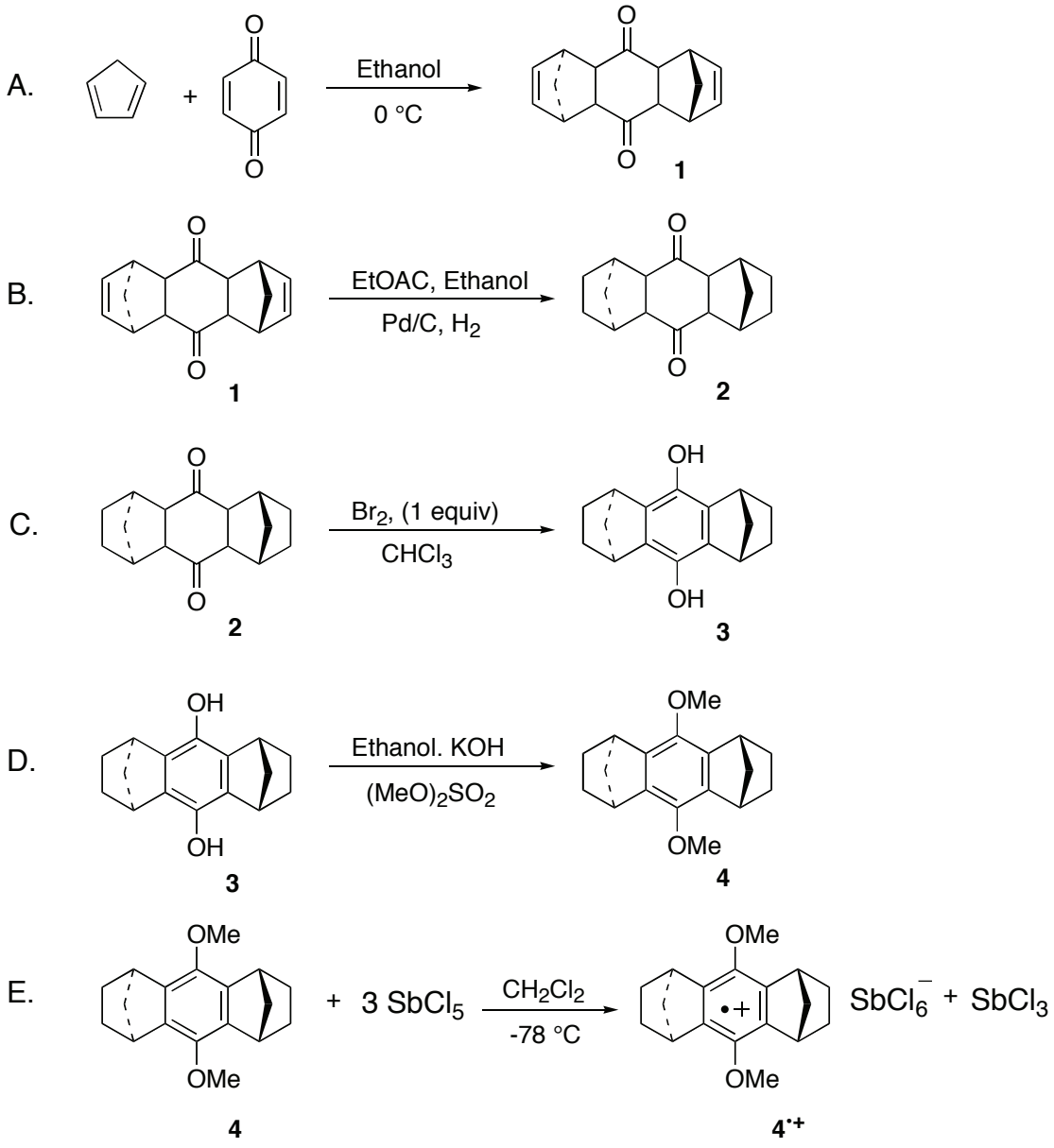
# PREPARATION OF 1,4:5,8-DIMETHANO-1,2,3,4,5,6,7,8-OCTAHYDRO-9,10-DIMETHOXYANTHRACENIUM HEXACHLOROANTIMONATE ($4^{+\bullet}SbCl_6^-$): A HIGHLY ROBUST RADICAL-CATION SALT

## [1,4:5,8-Dimethanoanthracene, 1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxy-, radical ion(1+), hexachloroantimonate(1-)]




Submitted by Rajendra Rathore,[1] Carrie L. Burns, and Mihaela I. Deselnicu.
Checked by Scott E. Denmark and Tommy Bui.

## 1. Procedure

*A. 1,4:5,8-Dimethano-1,4,4a,5,8,8a,9a,10a-octahydroanthracene-9,10-dione (**1**).* To a 500-mL conical flask is added *p*-benzoquinone (10.8 g, 100 mmol) [Note 1] and absolute ethanol (100 mL). The mixture is stirred at room temperature for 10 min and then is cooled in an ice-salt bath (ca. –5 °C, external). [Note 2] Freshly cracked cyclopentadiene (13.2 g, 200 mmol) [Note 3] is added slowly via syringe over 3-5 min and the resulting mixture is stirred in the ice-salt bath for 20 min and then for an additional 30 min at room temperature. A large amount of the adduct **1** precipitates during the course of the reaction. [Note 4] The resulting slurry is cooled in an ice bath (ca. 0 °C, external) and the precipitate is filtered using a Büchner funnel and is washed with ice-cold ethanol to yield 20.9-21.6 g (87-90%) of cycloadduct **1** as a nearly colorless, crystalline solid [Note 5].

*B. 1,4:5,8-Dimethanododecahydroanthracene-9,10-dione (**2**).* A solution of diketone **1** (19.2 g, 80 mmol) in a mixture of ethanol (50 mL) and ethyl acetate (250 mL) is combined with 10% Pd-C (200 mg) in a 500-mL pressure bottle [Note 6]. The bottle is pressured to 60 psi of hydrogen and shaken on a Parr apparatus for three hours (when the uptake of hydrogen ceases) [Note 7]. The mixture is then diluted with dichloromethane (~200 mL) to dissolve the precipitate and the solution is filtered *in vacuo* through a short pad of Celite (100 g) in a sintered glass funnel. The Celite pad is washed with dichloromethane (3 x 150 mL) and the colorless solution is concentrated on a rotary evaporator to afford diketone **2** (18.8 g, 96%) as a white solid. [Note 8]

*C. 1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydroanthracene-9,10-diol (**3**).* In a 500-mL, three-necked, round-bottomed flask equipped with a 125-mL pressure-equalizing addition funnel and nitrogen inlet and outlet adapters, is placed diketone **2** (18.3 g, 75 mmol) and anhydrous chloroform (75 mL). [Note 9] A solution of $Br_2$ (12.0 g, 75 mmol) in chloroform (75 mL) was placed in the dropping funnel and was added dropwise over 0.5 h under a slow stream of nitrogen at room temperature. [Note 10] Stirring the reaction mixture while purging the flask with nitrogen is continued for another hour to remove the gaseous HBr. The resulting suspension is cooled in an ice-salt bath (approx. -5 °C) and is filtered *in vacuo* using a Büchner funnel. The solid is washed with ice-cold chloroform (2 x 25 mL) and is suction dried to

afford 17.4 g (96 %) of hydroquinone **3** as a colorless powder, which is used in the next step without further purification.

*D. 1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxy-anthracene (**4**).* A solution of hydroquinone **3** (16.9 g, 70 mmol) in absolute ethanol (175 mL) is placed in a three-necked, 500-mL, round-bottomed flask equipped with a pressure-equalizing addition funnel and nitrogen inlet and outlet adapters. To this mixture is added a solution of KOH (8.7 g, 155 mmol) in water (8.7 mL) followed by a solution of sodium hydrosulfite (2 g) in water (10 mL) under an inert atmosphere. Dimethyl sulfate (19.6 g, 155 mmol) is placed in the addition funnel and is then added dropwise over 30 min. After the addition is complete, the addition funnel is replaced with a condenser and the mixture is heated to reflux in a 120˚C oil bath for 3 h and then is cooled to room temperature. A second portion of KOH (2.0 g, 35 mmol, 0.5 equiv) is added to the flask followed by the dropwise addition of a second portion of dimethyl sulfate (4.4 g, 35 mmol, 0.5 equiv) through a 25-mL addition funnel. The addition funnel is replaced with a condenser and the mixture is heated for one hour and then is allowed to cool to room temperature. The reaction mixture is diluted with water (250 mL) and then is extracted with dichloromethane (3 x 100 mL). The combined dichloromethane extracts are successively washed with 10% aqueous NaOH solution (50 mL), water (100 mL), brine (50 mL), and then are dried over anhydrous magnesium sulfate. Removal of solvent *in vacuo* affords a crude material that is purified by filtration through a short column of silica gel (200 g) as follows. A solution of the crude product in a 25:1 mixture of hexanes and ethyl acetate (90 mL) is eluted through the silica gel column followed by an additional 900 mL of hexane/ethyl acetate, 25:1. The product-containing fractions are concentrated on a rotary evaporator to afford dimethyl ether **4** (15.3 g, 81%) as a cream colored solid [Notes 11 and 12].

*E. Preparation of* $\boldsymbol{4^{+\bullet}SbCl_6^-}$. A solution of hydroquinone ether **4** (2.7 g, 10 mmol) in anhydrous dichloromethane (20 mL) [Note 13] is placed in a 100-mL, three-necked, round-bottomed flask equipped with a 50-mL pressure-equalizing addition funnel and nitrogen inlet and outlet adapters. The addition funnel is charged with a 1.0 M solution of $SbCl_5$ in dichloromethane (15 mL,15 mmol) [Note 14] and the flask is cooled in a dry ice-acetone bath (approximately –75 °C, external). The $SbCl_5$ solution is slowly added (3-5 min) under a flow of nitrogen. The reaction mixture

immediately turns red and a large amount of dark-red material precipitates. The resulting mixture is warmed to 0 °C over 5-10 min, and anhydrous diethyl ether (50 mL) is added to precipitate the dissolved $\mathbf{4}^{+\bullet}SbCl_6^-$ salt. The dark-red microcrystalline precipitate is suction filtered using a medium-porosity sintered-glass funnel under a blanket of dry nitrogen and is washed with dry diethyl ether (2 x 20 mL). [Note 15] The salt is dried *in vacuo* at room temperature to afford $\mathbf{4}^{+\bullet}SbCl_6^-$ (5.6 g, 93%) as a red, crystalline solid. [Notes 16 and 17]

## 2. Notes

1. *p*-Benzoquinone, 98% was purchased from Aldrich Chemical Co. and was used without further purification.

2. *p*-Benzoquinone, generally, precipitates upon cooling and it dissolves eventually as the cycloaddition reaction proceeds.

3. Cyclopentadiene is prepared by heating commercial dicyclopentadiene (available from Aldrich Chemical Company, Inc.) at 160 °C in a distillation apparatus. Cyclopentadiene distills smoothly at 39–45 °C. For a detailed procedure, see: Moffett, R. B. *Org. Synth*., *Coll. Vol. IV*, **1963**, 238.

4. This adduct can be directly hydrogenated (using a Parr hydrogenation apparatus) after dissolving the precipitate by adding 200-mL ethyl acetate and 10% Pd-C (200 mg, Aldrich Chemical Co.); however, a longer hydrogenation time is required. Furthermore, a less pure product which required recrystallization was afforded. A simple filtration of the adduct **1** followed by its hydrogenation (as described in the procedure above) yields a colorless solid of high purity.

5. The spectral data for 1,4:5,8-dimethano-1,4,4a,5,8,8a,9a,10a-octahydroanthra-cene-9,10-dione (**1**) are as follows: mp 157-158 °C; $^1$H NMR ($CDCl_3$) δ 1.29 (br d, 2 H, $J$ = 8.6), 1.45 (dt, 2 H, $J$ = 8.6, 1.72), 2.87 (br, 4 H), 3.35 (br, 4 H), 6.18 (t, 4 H, $J$ = 1.7); $^{13}$C NMR ($CDCl_3$) δ 48.2, 49.5, 53.2, 136.4, 212.7.

6. A standard hydrogenation bottle purchased from ACE glass Inc. was used.

7. The hydrogenation can also be carried out at atmospheric pressure as well.

8. The spectral data for 1,4:5,8-dimethanododecahydroanthracene-9,10-dione (**2**) are as follows: mp 226-229 °C (decomp.); $^{1}$H NMR ($CDCl_3$) δ 1.25-1.30 (m, 4 H), 1.38-1.45 (m, 4 H), 1.38-1.58, (m, 4 H), 2.80 (br, 4 H), 2.86 (br, 4 H); $^{13}$C NMR ($CDCl_3$) δ 25.0, 39.2, 43.7, 53.6, 214.5.

9. Ethanol-free, anhydrous chloroform, which can be readily prepared according to the procedure from Perrin,[9] is recommended for this step. Anhydrous dichloromethane can also be used as the solvent for the bromination.

10. The nitrogen outlet was connected to gas-wash bottle containing a 20% (w/w) solution of sodium hydroxide.

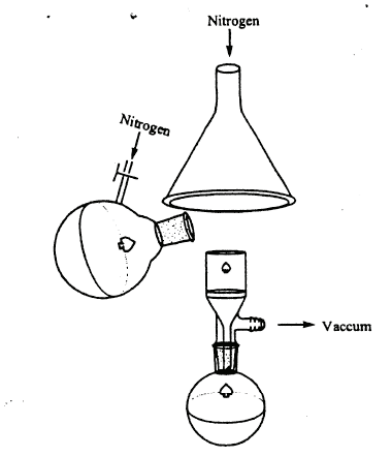
11. The spectral data for 1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxyanthracene (**4**) are as follows: mp 116-117 °C (decomp.); $^{1}$H NMR ($CDCl_3$) δ 1.15-1.19 (m, 4 H), 1.42-1.44 (br d, 2 H, $J$ = 8.55), 1.66-1.69 (m, 2 H), 1.87 (br d, 4 H, $J$ = 7.33), 3.54 (m, 4 H), 3.83 (s, 6 H); $^{13}$C NMR ($CDCl_3$) δ 27.0, 40.6, 48.9, 61.3, 137.5, 143.5.

12. The submitters described recrystallization of **4** by dissolving 10 g in boiling hexanes (150 mL) and allowing the product to precipitate by standing at room temperature overnight.

13. Anhydrous dichloromethane was obtained according to the procedure of Perrin.[9]

14. A 1 M solution of antimony pentachloride in dichloromethane can be purchased from Aldrich Chemical Co. This solution can also be prepared by dissolving neat $SbCl_5$ in anhydrous dichloromethane.

15. A large inverted funnel, connected to a nitrogen outlet, positioned above the sintered glass funnel is generally sufficient for maintaining an inert atmosphere during filtration of the cation radical salt (see sketch of the apparatus below).



16. The spectral data of [$\mathbf{4}^{+\cdot}$ $SbCl_6^-$]: UV-vis (dichloromethane), $\lambda_{max}$ = 518 and 486 (shoulder) nm, extinction coefficient, $\varepsilon_{518}$ = 7300 $M^{-1}$ $cm^{-1}$. Anal. calcd. for $C_{18}H_{22}O_2$ $SbCl_6$: C, 35.74, H, 3.67, Cl, 35.17. Found: C, 35.64, H, 3.54, Cl, 34.16. The pure cation-radical salt ($\mathbf{4}^{+\bullet}SbCl_6^-$) is >99% can be stored in a glass bottle at ambient temperatures indefinitely. The purity of the $\mathbf{4}^{+\bullet}SbCl_6^-$ salt can be confirmed by iodimetric titration as follows. Thus, a solution of $\mathbf{4}^{+\bullet}$ $SbCl_6^-$ (60.45 mg, 0.01 M) in anhydrous dichloromethane was added to a dichloromethane solution containing excess tetra-*n*-butylammonium iodide (1 mmol, 0.1 M) at 22 °C, under an argon atmosphere, to afford a dark brown solution. The mixture was stirred for 5 min and was titrated (with rapid stirring) by a slow addition of a standard aqueous sodium thiosulfate solution (0.005 M) in the presence of a starch solution as an internal indicator. Based on the amount of thiosulfate solution consumed (58.6 mL), purity of the cation radical was determined to be ca. 98.5%. Moreover, the purity can also be estimated by utilizing the spectrophotometric data as follows. Thus, a known quantity of $\mathbf{4}^{+\bullet}SbCl_6^-$ was dissolved in anhydrous dichloromethane and the absorbance was monitored at 518 nm using a 1-cm quartz cuvette. For example, a solution of 3.0 mg of $\mathbf{4}^{+\bullet}SbCl_6^-$ in 30 mL anhydrous dichloromethane showed an absorbance of 1.20 at 518 nm (actual concentration = 1.64 x $10^{-4}$ M, 99.6% pure). The actual concentration of the $\mathbf{4}^{+\bullet}SbCl_6^-$ was calculated by using the equation: Absorbance at 518 nm/7300 = actual concentration.

17. The radical cation salt $\mathbf{4}^{+\bullet}SbCl_6^-$ was also characterized by ESR spectroscopy. A solution of the salt (2 mg, 3.3 μmol) in 30 mL of dichloromethane was prepared in a dry box in a flame-dried, 50-mL round-bottomed flask. The solution was filtered through filter paper to remove particulates. About 0.25-0.35 mL of this solution was placed in a dry ESR tube under argon. The tube was sealed with a septum and the spectrum was recorded. G = 2.0046; $A_1$ = 3.3 Gauss (6H), $A_2$ = 2.1 Gauss (2H), $A_3$ = 1.2 Gauss (2H).

## Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

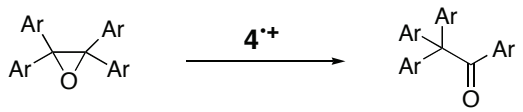
## 3. Discussion

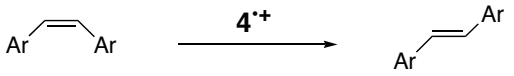
The hydroquinone ether **4** is an electron-rich molecule ($E^{o}_{ox}$ = 1.11 V vs. SCE) that is readily oxidized to a remarkably stable cation-radical salt, which can be stored as a crystalline solid for an indefinite period. Stable radical-cation salts are of fundamental importance to organic materials science because they constitute the smallest units that carry both a delocalized positive charge and an unpaired electron. Thus, radical-cation salts provide the basis for experimentation in conductivity and ferromagnetism, etc. Radical cations are important intermediates in a rich menu of organic transformations.[2] They are also useful as electron-transfer catalysts[3] in a variety of organic and organometallic transformations, as well as tools for elucidation of electron transfer mechanisms.

Removal of an electron from a neutral molecule leads to an "umpolung" of the normal reactivity character. The cation radical possesses greatly enhanced electrophilic reactivity (due to the cationic charge), as well as homolytic reactivity (due to the radical character). Radical cations can promote a variety of unimolecular and bimolecular reactions as illustrated by following examples.[2]

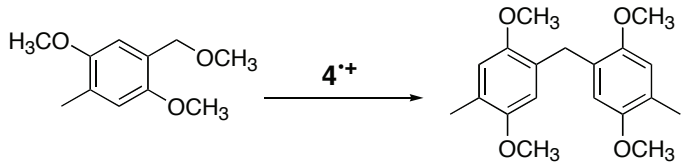
In addition, the ready availability of $\mathbf{4}^{+\bullet}$ allows its utilization for the formation of cation radicals from a variety of organic donors for spectroscopic monitoring, as well as for the elucidation of electron transfer mechanisms.[3f,3g]

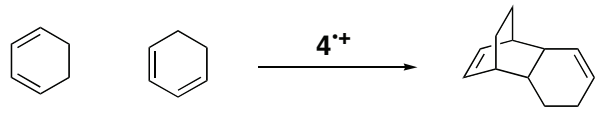
The method described here for the preparation of $\mathbf{4}^{+\bullet}$ is essentially a detailed description of our recently published procedure.[4] To date, the only radical cation salts readily accessible to organic chemists are the heteroatom-centered *tris*(4-bromophenylaminium)[5] and thianthrenium[6] salts. It is envisioned that the ready availability of **4** and its cation radical $\mathbf{4}^{+\bullet}$ will foster its use in a variety of organic and organometallic syntheses,[3,7] as well as in the exploration of the role of single electron transfer (SET) in various chemical processes.[2,8]

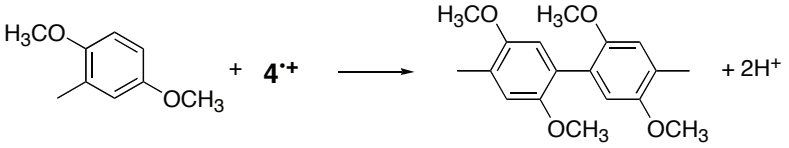



(Ar = Anisyl or 2,5-dimethoxy-4-methylphenyl)





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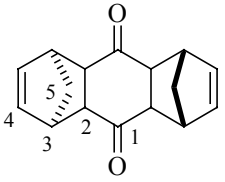
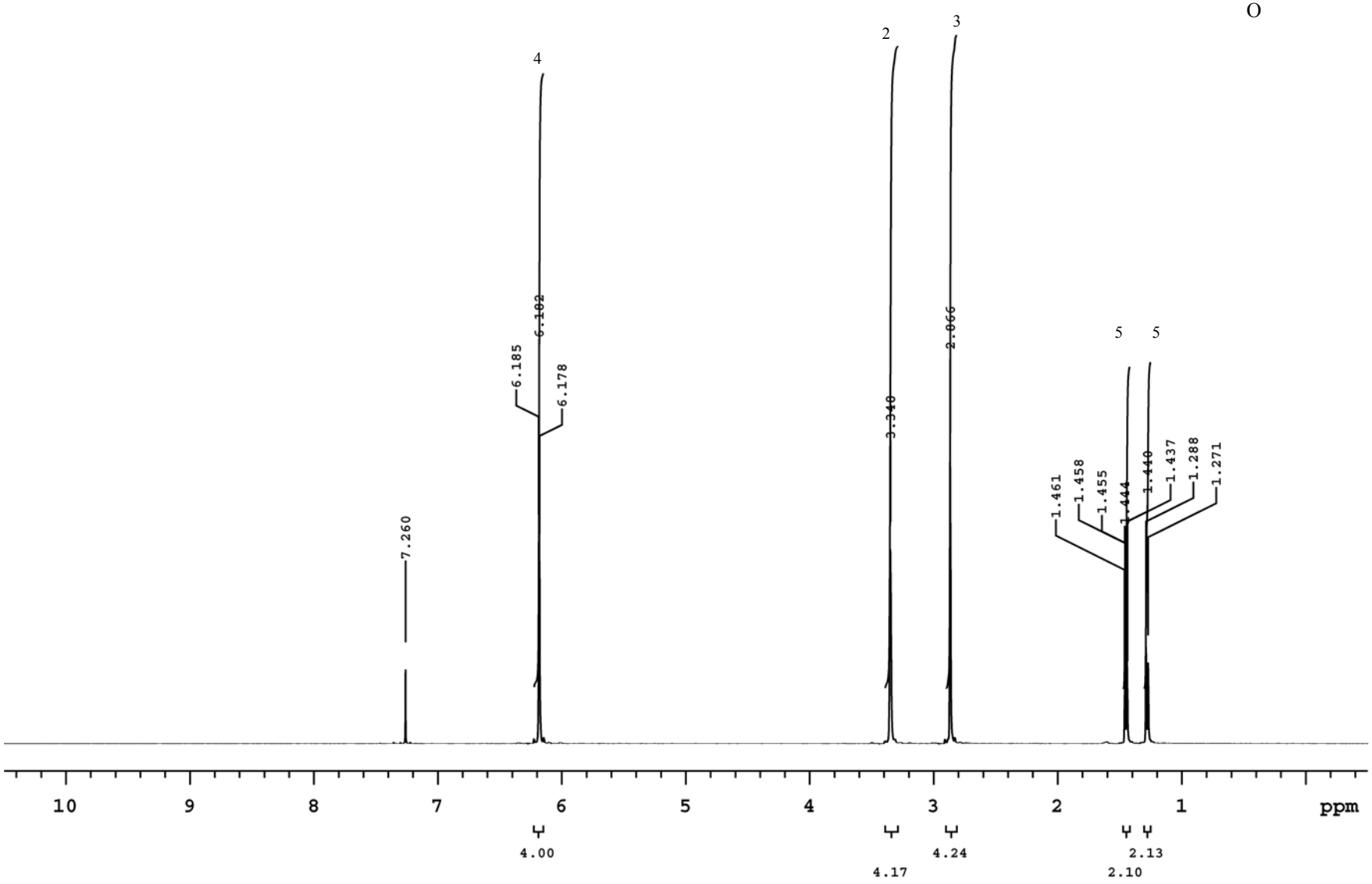
**9**. Perrin, D. D.; Armarego, W. L. F.; Perrin, D.R. *Purification of Laboratory Chemicals, 2nd Ed*.; Pergamon: New York, 1980.

## Appendix
## Chemical Abstracts Nomenclature (Registry Number)

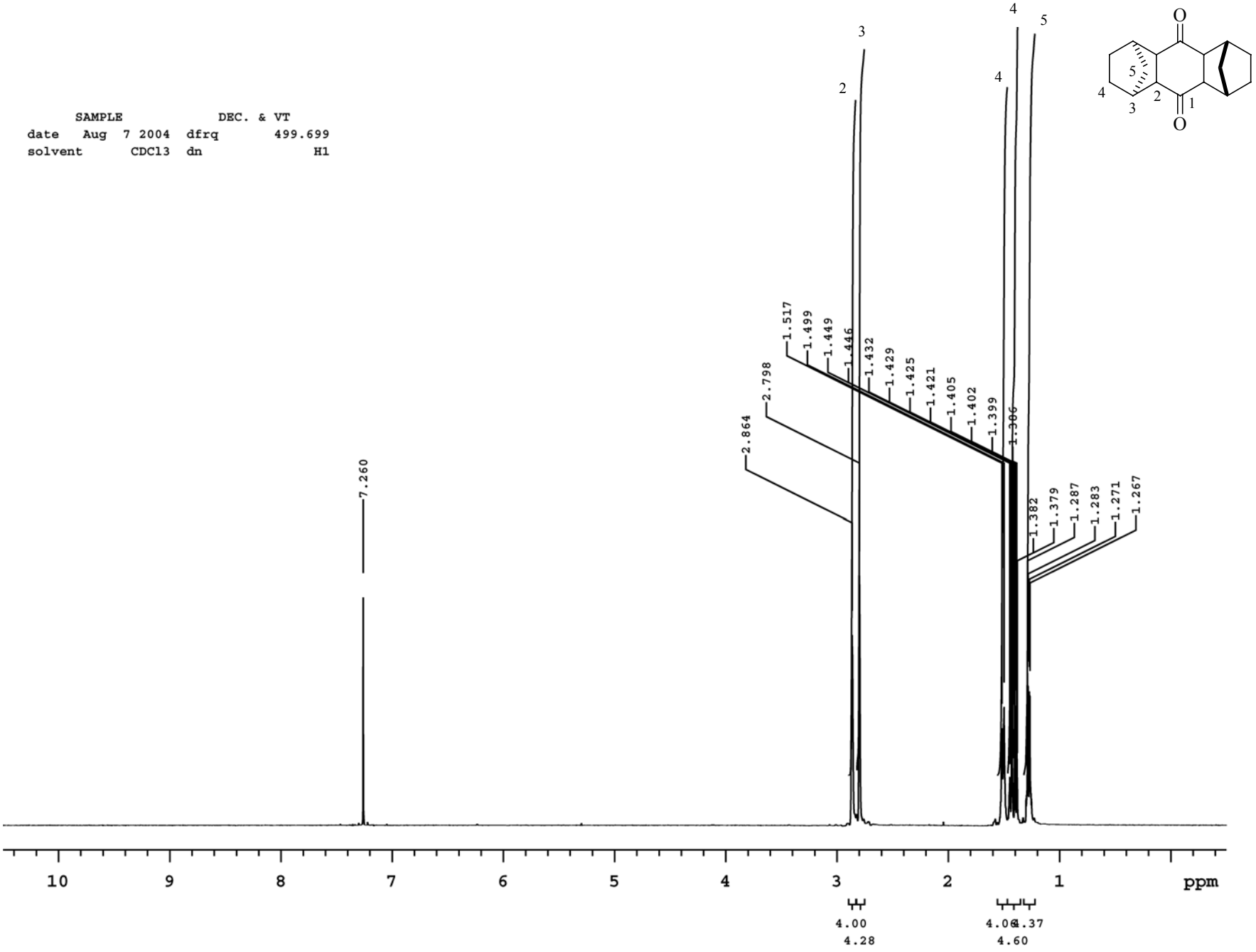
p-Benzoquinone: 2,5-Cyclohexadiene-1,4-dione; (106-51-4)
Cyclopentadiene: 1,3-Cyclopentadiene; (542-92-7)
1,4:5,8-Dimethano-1,4,4a,5,8,8a,9a,10a-octahydroanthracene-9,10-dione: 1,4:5,8-Dimethanoanthracene-9,10-dione, 1,4,4a,5,8,8a,9a,10a-octahydro-, (1*R*,4*S*,4a*R*,5*S*,8*R*,8a*S*,9a*S*,10a*R*)-; (78548-82-0)
1,4:5,8-Dimethanododecahydroanthracene-9,10-dione: 1,4:5,8-Dimethanoanthracene-9,10-dione, dodecahydro-, (1**a**,4**a**,4a**a**,5**b**,8**b**,8a**b**,9a**a**,10a**b**)-; (2065-48-7)
Bromine; (7726-95-6)
1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydroanthracene-9,10-diol: 1,4:5,8-Dimethanoanthracene-9,10-diol, 1,2,3,4,5,6,7,8-octahydro-, (1**a**,4**a**,5**b**,8**b**)-; (130778-68-6)
Potassium hydroxide; (1310-58-3)
Sodium hydrogen sulfite: Sulfurous acid, monosodium salt: (7631-90-5)
Dimethyl sulfate: Sulfuric acid, dimethyl ester; (77-78-1)
1,4:5,8-Dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxy-anthracene: 1,4:5,8-Dimethanoanthracene, 1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxy-, (1*R*,4*S*,5*S*,8*R*)-; (322733-47-1)
Antimony pentachloride; Antimony chloride; (7647-18-9)

Cycloadduct **1**



Dione **2**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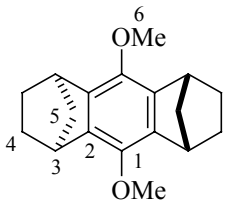
Dimethoxyanthracene **4**

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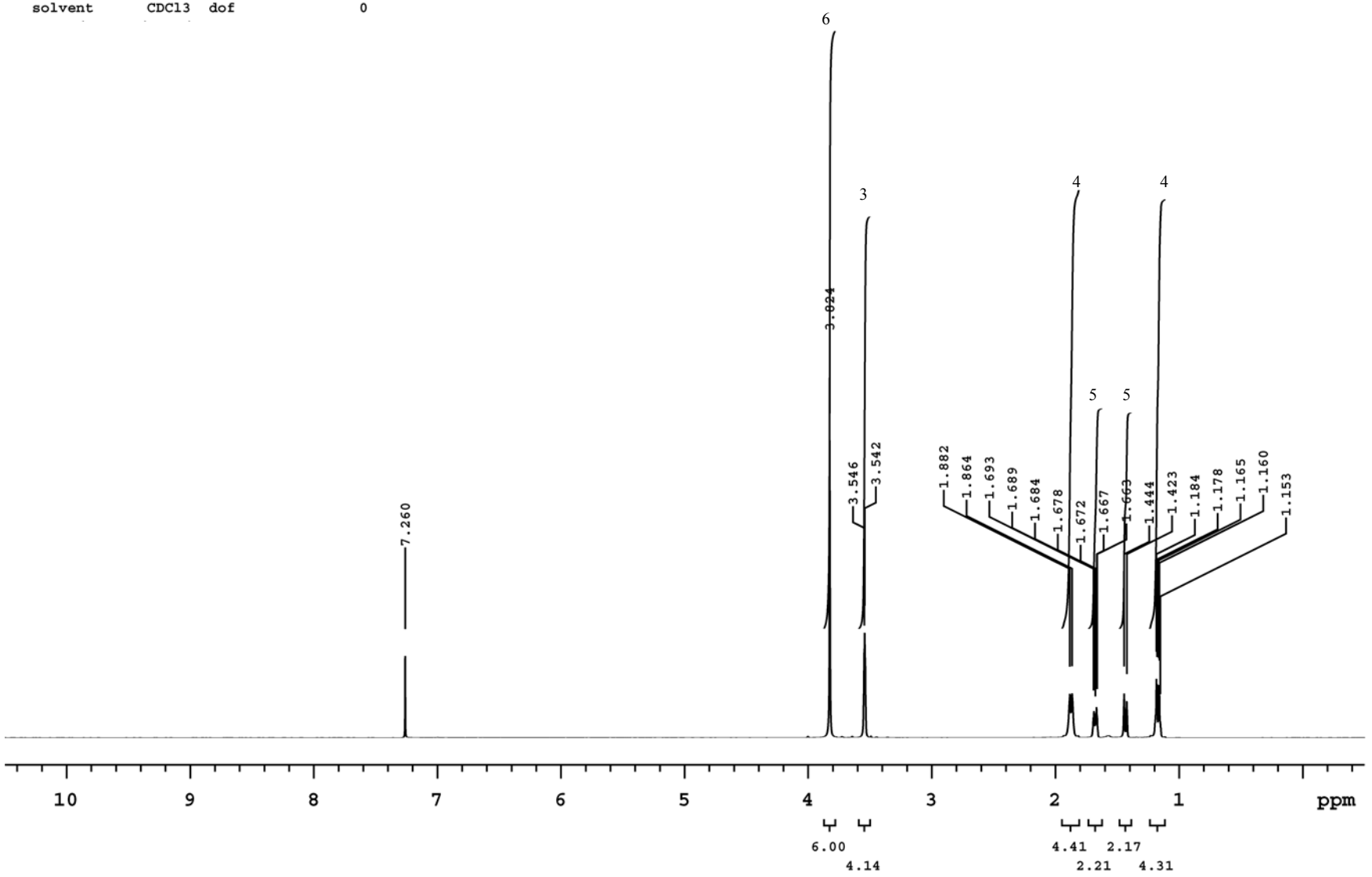
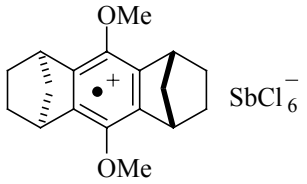
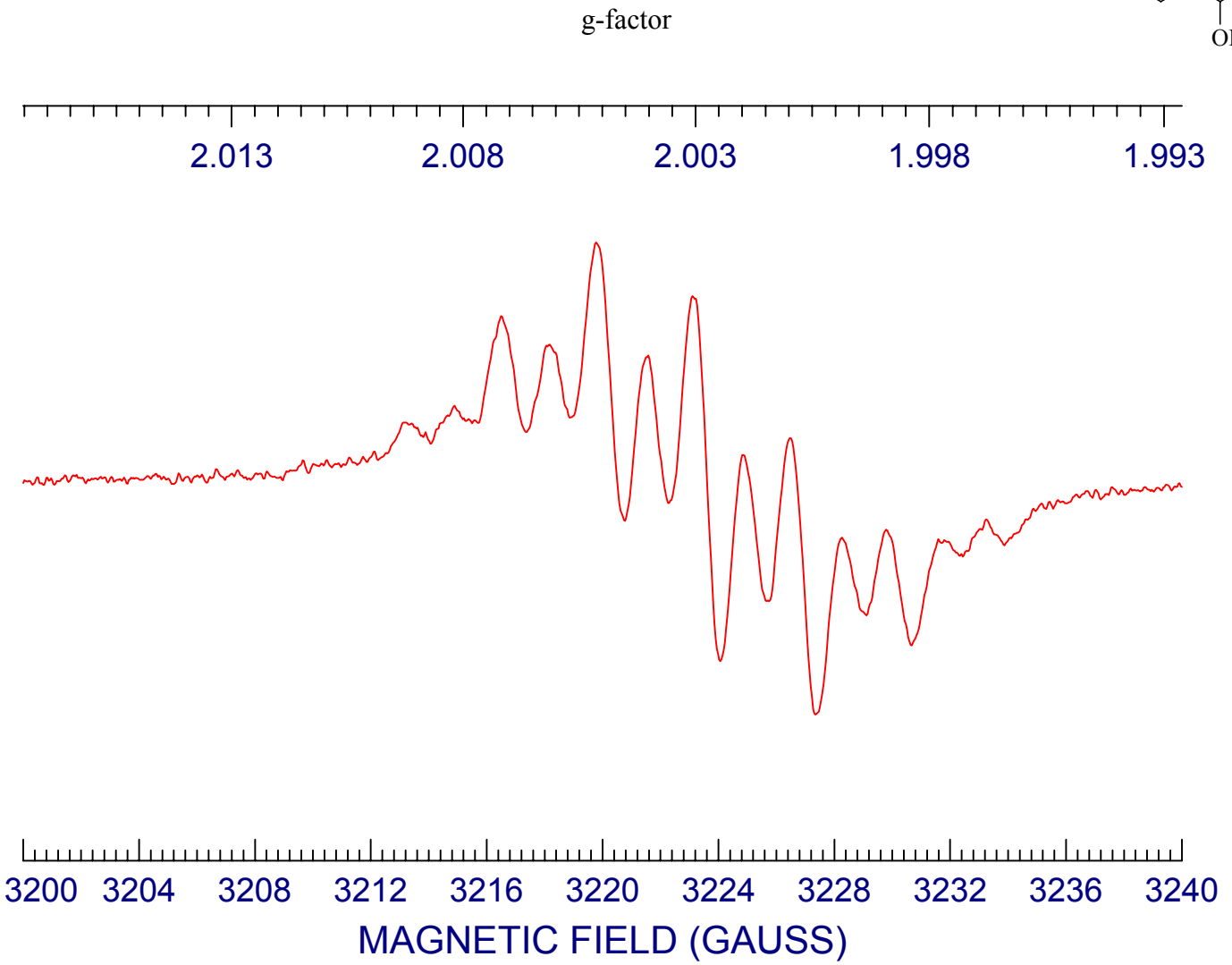
solvent CDCl3 dof 0



Radical cation $4^{+\cdot}$



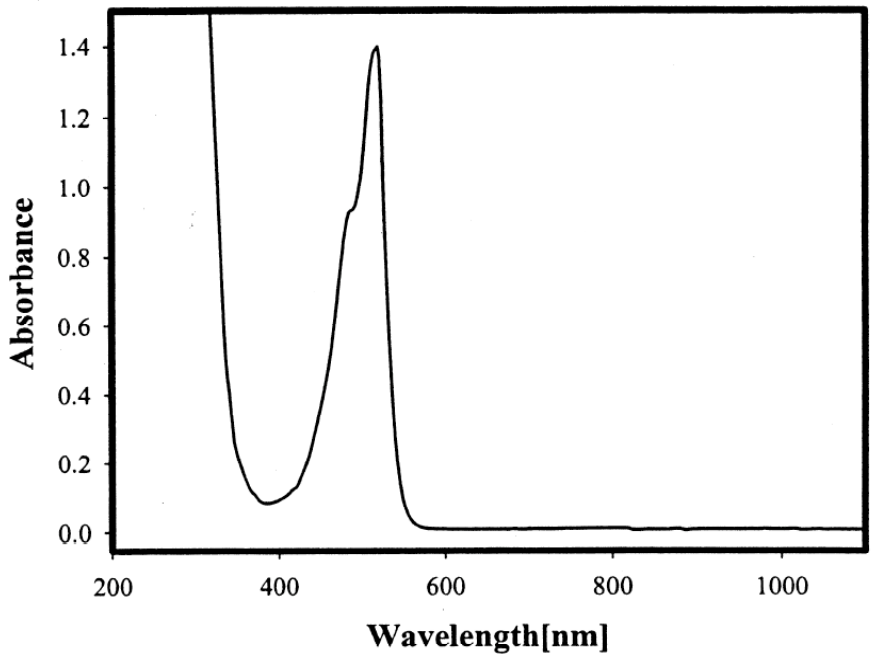



**Figure 1.** A UV-vis absorption spectrum of $1.92 \times 10^{-4}$ M $\mathbf{4}^{+\bullet}$ $SbCl_6^-$ in dichloromethane at 22 °C.

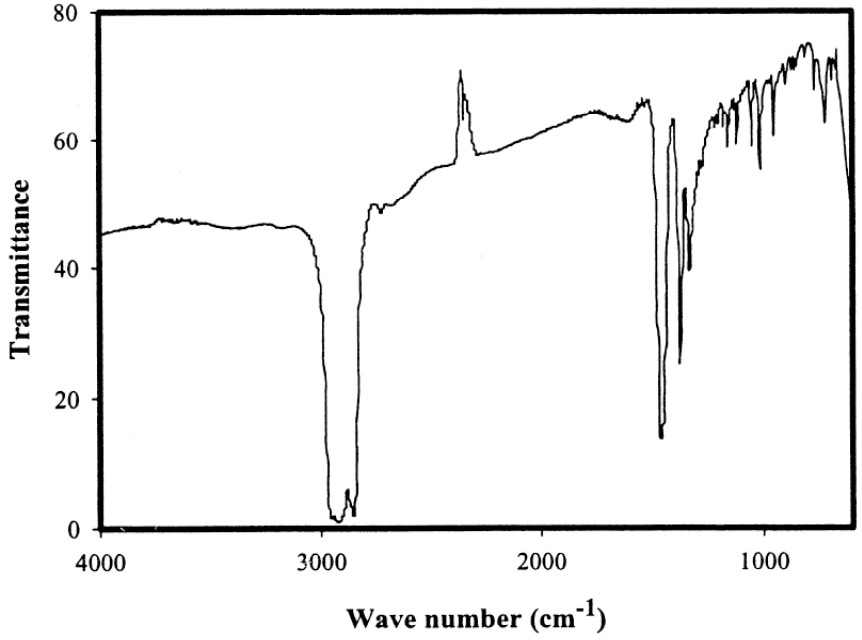



**Figure 2.** An infrared spectrum of crystalline $\mathbf{4}^{+\bullet}$ $SbCl_6^-$ in nujol at 22 °C.