THE UNIVERSITY OF MANITOBA

THE SYNTHESIS OF SPECIFICALLY DEUTERATED ANTHRACENES

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

WINNIPEG, MANITOBA

OCTOBER 1973

ABSTRACT

Synthetic methods for the preparation of anthracene-9,10-d_2, -1,4-d_2, -2,3-d_2, -1,4,5,8-d_4, -2,3,6,7-d_4, and -1,2,3,4-d_4 are described.

ACKNOWLEDGEMENTS

I wish to express my gratitude to the following people for their assistance in preparing this thesis.

To Dr. Jim Charlton for his patience and guidance, and for suggesting the problem;

To Marv Arneson for running the numerous mass spectra;

To the Graduate Research Fund, University of Manitoba, for financial support;

To Dr. C. J. Macdonald, for the time I took to complete the thesis, while in his employ;

To my wife, Kisanya, for her encouragement.

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INTRODUCTION

For several years, workers have been interested in the physical and chemical processes occurring in molecules brought about by the absorption of light. Early investigators devoted their efforts to simply finding out what chemical changes were initiated by light. In later years, workers devoted their efforts to investigation of the actual mechanisms of interaction between light and matter. Of greatest interest was the interaction of matter with ultraviolet and visible light, although much study has been made in other areas of spectroscopy. Most photochemical and photophysical studies were performed on unsaturated organic compounds, many of these being aromatic. In particular, in recent years, anthracene has been a major compound used in the measurement of optical properties of molecules. As a result, much effort has been dedicated to its synthesis and purification (1-5).

It has been known for some time that substitution of atoms in molecules with their heavier isotopes slows down non-radiative transitions in electronically excited molecules. This phenomenon has been the experimental basis for verifying mechanisms of such non-radiative processes, and hence the synthesis of isotopically substituted compounds is of current interest. The usual procedure has

been to substitute hydrogen atoms by deuterium to determine whether the excited species relaxed more slowly or not. In particular, interest has been shown in the triplet lifetimes of specifically deuterated compounds (6). Because of such a theoretical interest (7) in the position-dependent deuterium effects on the triplet lifetime of anthracene, it became necessary to devise synthetic routes for the preparation of the following compounds:

Anthracene-9,10-d_2.....1

Anthracene-1,4-d_2.....2

Anthracene-1,4,5,8-d_4.....3

Anthracene-2,3-d_2.....4

Anthracene-2,3,6,7-d_4.....5

Anthracene-1,2,3,4-d_4.....6

The above compounds could also be of use in verifying the calculations performed by Cyvin and Cyvin (8) on the mean amplitudes of vibration of compounds 3 and 5, and an extension of their calculations might result.

The use of deuterium and C^{13} labelling of organic molecules has often helped to explain the mechanisms of fragmentation of such molecules under electron impact in mass spectrometry. In some molecules, partial or complete scrambling of the hydrogen and/or carbon atoms occurs prior to fragmentation. That is, under electron impact, all or

some of the hydrogen and/or carbon atoms of a molecule can be rendered equivalent by some re-arrangement, the activation energy being supplied by the electron beam (9). It would be of interest to determine whether such randomization occurs in anthracene prior to fragmentation. Compounds 1 to 6 might be useful in such an investigation.

Before a synthetic route leading to these compounds was devised, a literature survey was undertaken to determine which had already been prepared. Laurent, Calas, and Josien (10) had reported the synthesis and infrared (IR) spectra of the three monodeutero anthracenes (anthracene-1-d, anthracene-2-d, anthracene-9-d) and the dideutero compound anthracene-9,10-d_2 (1). These authors mentioned that prior to their synthetic method, Gold and Long (11) had tried isotopic exchange of anthracene with D_2SO_4, which led to a mixture of mono- and polydeuterated anthracenes. Also, the reduction of anthrone with zinc dust and a solution of NaOH in a mixture of D_2O and H_2O (1:3) gave anthracene, and a mixture of 80% anthracene-9-d, and 20% anthracene-9,10-d_2 (1). Laurent et al claimed that their method, hydrolysis of the corresponding mono- and dimagnesium compounds with D_2O (99.25%) gave the desired deuterated anthracenes in good yield, giving only traces of non-deuterated anthracene.

Another method for the preparation of 1 was given by Petukhov and co-workers (12). 9,10-dibromo anthracene was treated with butyl lithium to give 9,10-dilithioanthracene, which was subsequently decomposed with D_2O to give a mixture of isotopic anthracenes containing 73% 1.

Brown and Cookson (13) reported a preference for Petukhov's method for the synthesis of 1 and anthracene-9-d,

because of the non-specificity of the D_2SO_4 exchange method (11), and the poor yield they obtained using the Grignard method (10). They reported obtaining better than 97% deuteration for anthracene-9-d and 90% deuteration for 1.

We found that Hoffman and Schmid (14) and Chafik and Mecke (15) also had studied the IR spectrum of 1. Hoffman and Schmid gave no synthesis for the compound. Chafik and Mecke prepared 1 by reacting 9,10-dibromoanthracene with zinc and deuterated acetic acid (CH_3CO_2D).

J. B. Pawliczek and co-workers (16,17) studied the nuclear magnetic resonance (NMR) spectrum of 1, which they had prepared by a method similar to that of Petukhov (12). A mass spectrum analysis showed 97.5% 1 and 2.5% anthracene-9-d. The above works (Figure I) were the only ones found referring to the preparation of 1, and none of the compounds 2 - 6 have been reported in the literature.

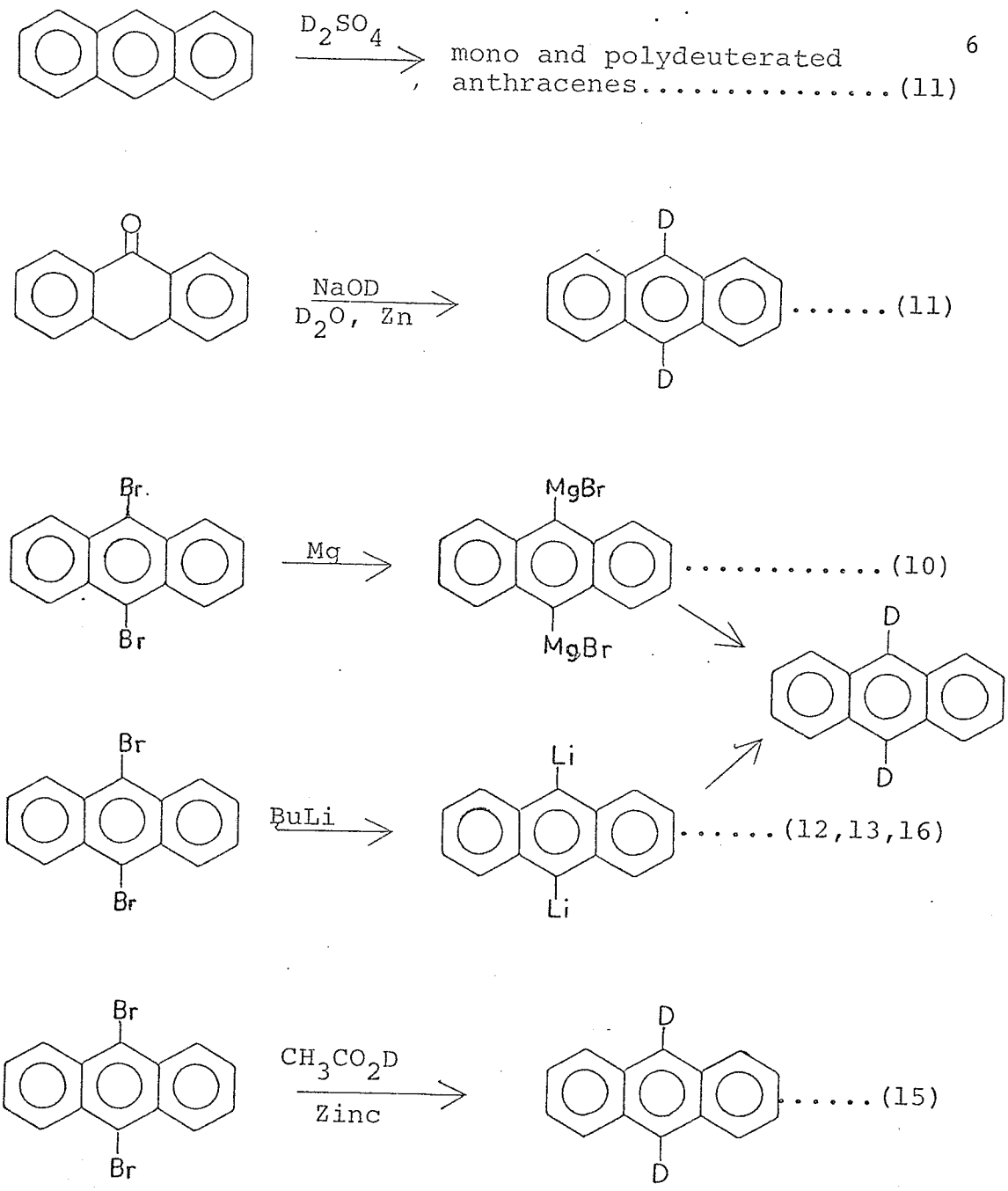


Figure I. Previous syntheses of anthracene-9,10-d_2 (1).

OTHER METHODS

The literature survey gave five alternate methods for the preparation of 1. The problem then was to devise a scheme for the preparation of compounds 2 - 6.

If the preparation of these deuterated anthracenes involved building up the carbon skeleton from smaller precursors, one could introduce the deuterium in either the final stage of the scheme, the initial stage of the scheme, or in some intermediate stage(s).

Method I

Metalation of the corresponding halogenated anthracene compounds, followed by hydrolysis with D_2O is an example of the first case. A grignard reaction on the halo compounds could be difficult, as was experienced by Brown and Cookson (13) with 9-bromoanthracene and 9,10-dibromoanthracene. Bachman and Kloetzel (18) had reported that under optimum conditions, the reaction of freshly prepared and cleaned magnesium turnings with very pure 9-bromoanthracene yielded only 86% of the theoretical yield of the Grignard reagent. Although Laurent et al (10) claimed to get good magnesium incorporation, it was necessary for them to use a special mixer which had been developed by Calas and Lalande (19).

The extent of magnesium incorporation into the anthracene skeleton would be lessened further by the fact that ortho di-Grignard reagents cannot be formed (20). This

problem would complicate the syntheses from 2,3-dihalo-, 2,3,6,7-tetrahalo-, and 1,2,3,4-tetrahalo anthracenes. The problem could possibly be remedied by carrying out the preparation of the Grignard reagent as quantitatively as possible, and the decomposing it with D_2O. Repetition of the Grignard preparation on the remaining halogen-containing molecules, followed again by decomposition with D_2O should eventually yield the desired compound (Figure II). The same procedure would be necessary for the analogous organolithium reactions.

Another problem however, is the possible formation of benzyne-like intermediates in the dehalogenation, as is experienced with ortho-halo lithiobenzene compounds. Craig and Fowler (21) also observed that considerable amounts of 1-butene-3-yne and 1,3-butadiyne were formed in the reductive dechlorination of hexachloro-1,3-butadiene to 1,3-butadiene with zinc and H_2O. However, they report that good yields of diene are observed when sodium iodide and/or cupric chloride are added to the reaction mixture in catalytic amounts. These or other catalysts might also prevent the formation of benzyne-like intermediates in the Grignard reactions or the lithioanthracene reactions. Should this method be chosen for the synthesis, it would be preferable to use the iodine or bromine substituted anthracenes, because the heavier halogens are more easily metalated.

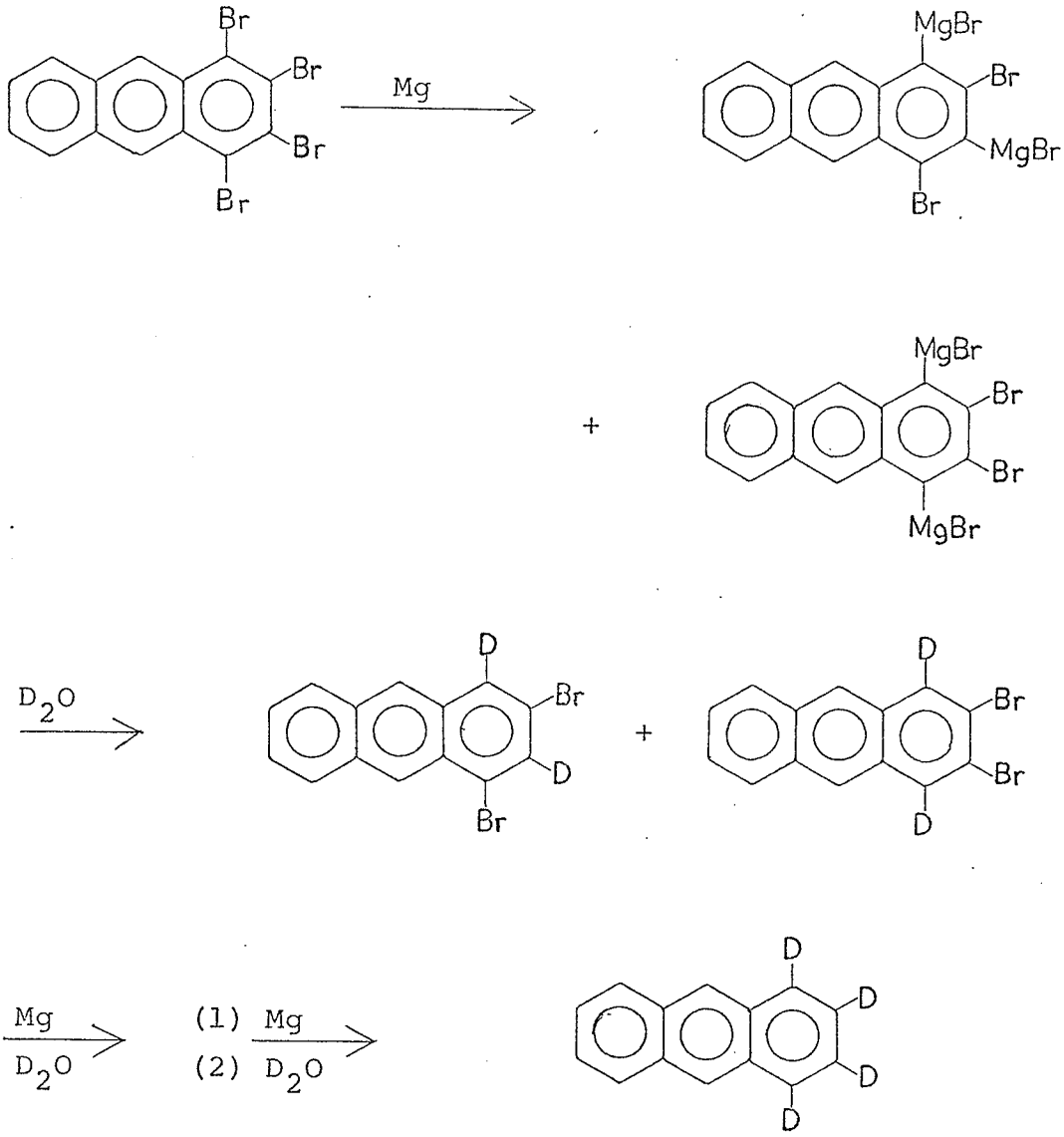


Figure II. Possible route to anthracene-1,2,3,4-d_4 (6).

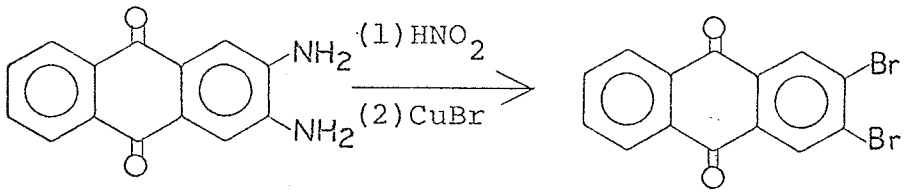
Preparation of halogenated anthracenes

The preparation of the halogenated anthracenes themselves would be necessary, because they are not all commercially available. In his book on carbon compounds (22), Rodd refers to Grandmougin (23) for the synthesis of 1,4-dibromoanthraquinone and 2,3-dibromoanthraquinone, and to Ullman and Billig (24) for the corresponding chloro compounds. These could be reduced to the corresponding anthracene derivatives by one of several available methods. Grandmougin obtained the compounds by diazotization of the corresponding aromatic amines followed by a Sandmeyer reaction. Ullman and Billig used the ortho-benzoylbenzoic acid synthesis (Figure III) for the preparation of the halogenated anthraquinones.

H. Schilling (25) prepared 1,4,5,8-tetrachloroanthraquinone by the sulfonation of 1,5-dichloroanthraquinone, followed by chlorination (Figure III).

A combination of the methods used by Grandmougin and by Ullman could lead to all of the necessary halogenated anthracenes (Figure IV). Halogen in the benzoic acid portion of the ortho-benzoylbenzoic acid makes condensation more difficult and sometimes impossible, but halogen in the phthalic acid half promotes condensation. Also, amino groups in the benzoic acid half strongly promote condensation.

The possibility of preparing the halogeno-anthraquinones



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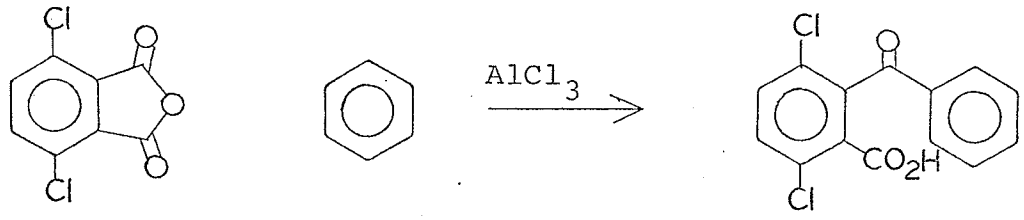

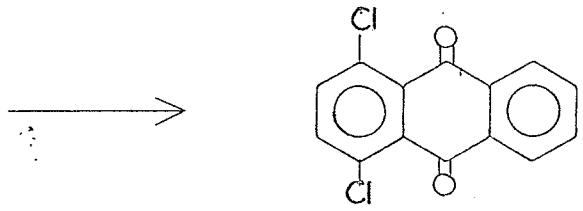

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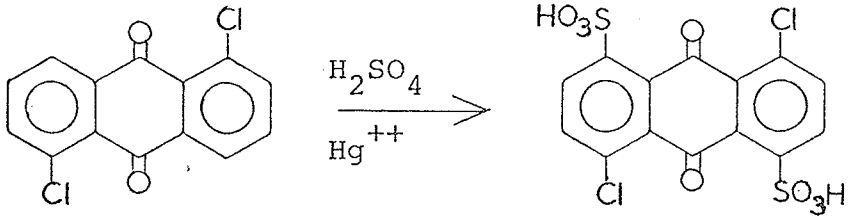

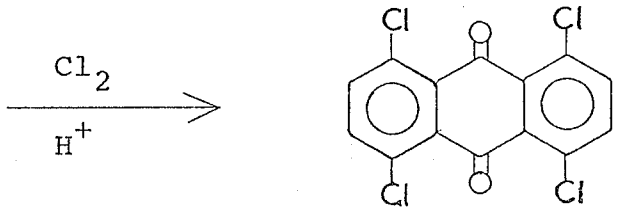

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Figure III. Previous syntheses of halogenated anthraquinones.

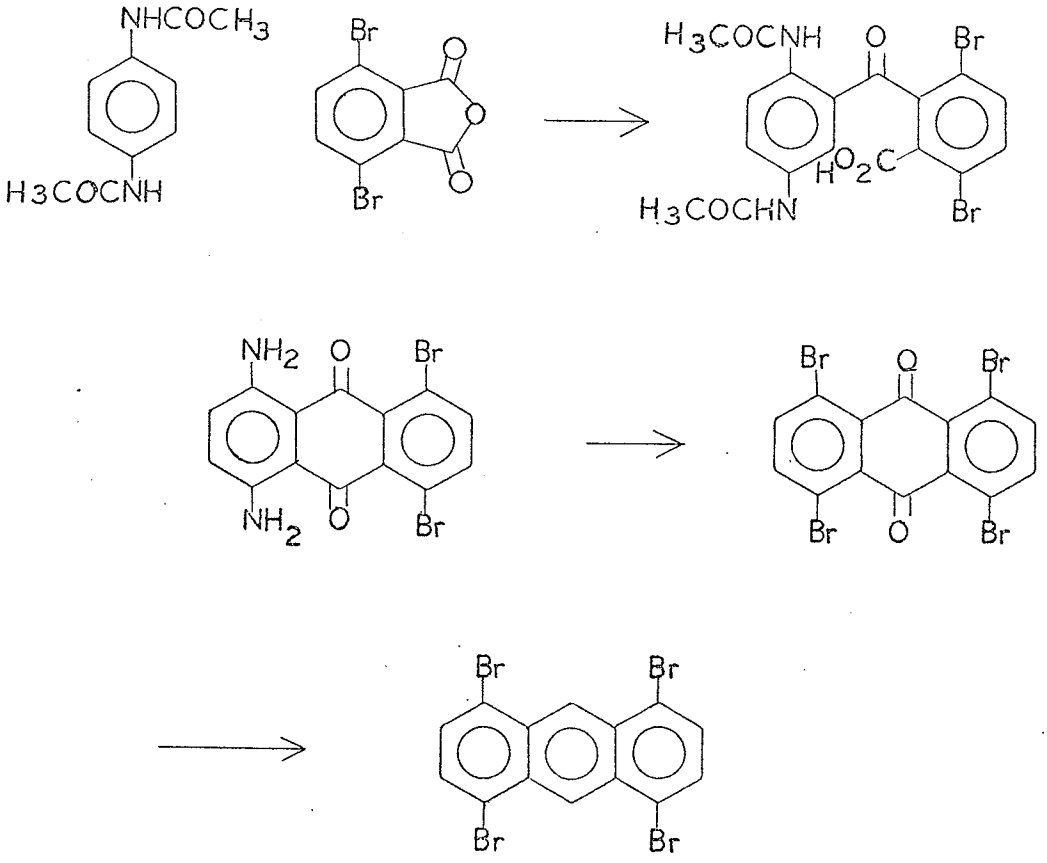


Figure IV. Possible synthesis of 1,4,5,8-tetrabromo anthracene.

from Diels-Alder reactions between halogeno-1,3-butadienes and quinones was considered. However, Coffman and Carothers (26) have reported that neither terminally halogen-substituted 1,3-butadienes, nor 2,3-dihalogeno-1,3-butadienes react with either 1,4-naphthoquinone or p-benzoquinone.

Preparation of the appropriate halogenated anthracenes has been shown to be a possible route to the desired deuterated anthracenes. However, it has also been shown that many difficulties could result from this method.

Method II

The deuterium could also be introduced into the carbon skeleton in the initial stages of the synthesis. In particular, the condensation of deuterated 1,3-butadienes with p-benzoquinone and 1,4-naphthoquinone is considered. Diels and Alder (27) and Alder and Stein (28) had reported obtaining non-deuterated anthraquinone by the above method (Figure V). The Diels-Alder adducts were oxidized to anthraquinone by treatment with chromium trioxide in acetic acid or with air and alcoholic KOH solution. Several methods are available for the reduction of anthraquinone to anthracene (29).

The necessary deuterated 1,3-butadienes have also all been previously prepared (Figure VI).

Craig and Fowler (21) reported the preparation of 1,3-butadiene-d_6 and 1,3-butadiene-2,3-d_2 by reductive

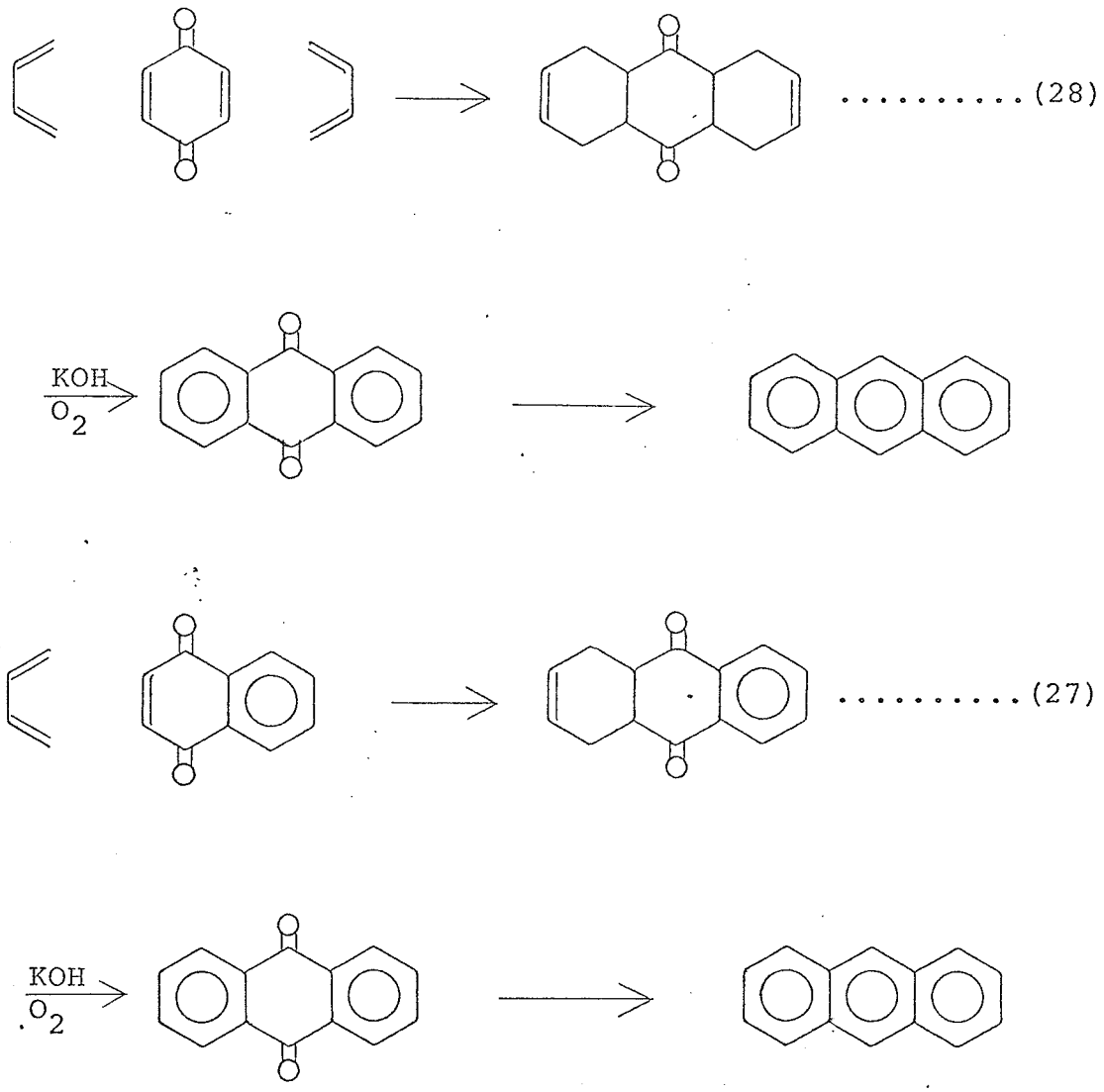


Figure V. Diels-Alder synthesis of Anthracene.

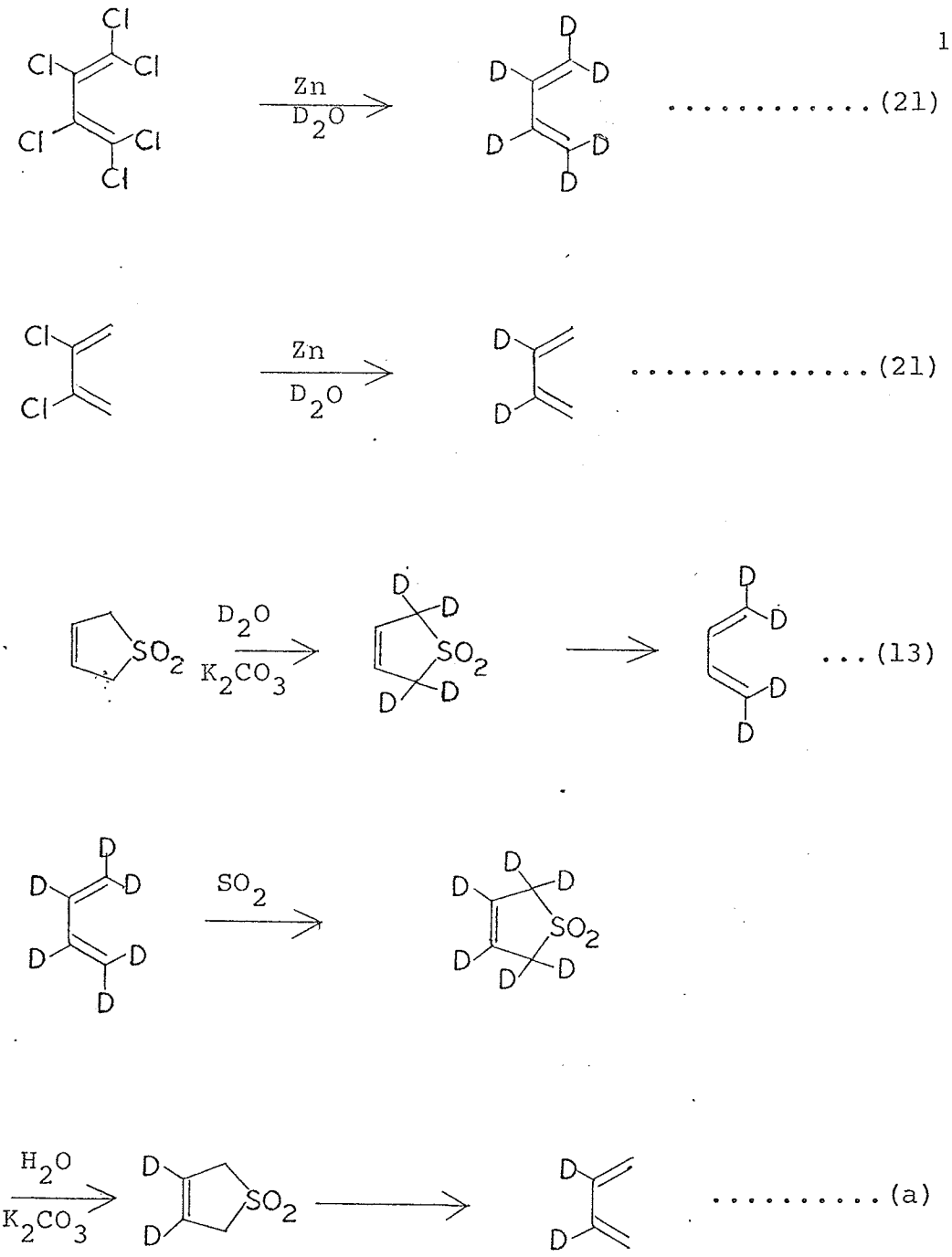


Figure VI. Syntheses of deuterated 1,3-butadienes.
a; See experimental.

dechlorination of the corresponding chloro compounds, with zinc and D_2O.

Cope, Berchtold, and Ross (30) obtained 1,3-butadiene-1,1,4,4-d_4 by repeated exchange of 3-sulfolene with D_2O and K_2CO_3, followed by thermal decomposition.

The Diels-Alder method for the preparation of the deuterated anthracenes is obviously shorter than the method utilizing the halogenated anthracenes. Another advantage is the fact that all of the reactions involved have been previously reported. One disadvantage, however, is the possible dilution and/or randomization of the deuterium label. When an isotopic label is introduced in an early stage of a synthetic scheme, there is a greater likelihood that this label will be partially lost or scrambled, than when the isotopic label is introduced at a later state of the scheme. This would not necessarily pose a threat to the suitability of the method. If a particular reaction tends to scramble hydrogen atoms within a molecule, another reagent could possibly be found to effect the same reaction.

No other scheme to build up the anthracene skeleton from deuterated precursors was considered, because of the relative simplicity of the above scheme, and also because of the fact that all of the necessary reactions for the above scheme had been previously reported in good yields.

DISCUSSION

After considering the possibilities, we chose these methods for the syntheses of the deuterated anthracenes. Of the available methods for the preparation of anthracene-9,10-d_2 (1), that of Petukhov (12) was initially chosen, because of the difficulty reported for the Grignard reaction (13), because of the non-specificity of the D_2SO_4 reaction (11), and also because we were not at that time aware of Chafik's method. The method involved treating 9,10-dibromoanthracene with n-butyl lithium in benzene to prepare the 9,10-dilithioanthracene. This was subsequently hydrolyzed with D_2O yielding the dideutero derivative.

The reaction was carried out several times, but the highest isotopic purity (mole % anthracene-9,10-d_2) was 88%, the remaining 12% being anthracene-9-d. In an attempt to improve the isotopic purity, a mild acid-catalyzed exchange reaction similar to Gold and Long's D_2SO_4 exchange method (11) was considered. Since the 9 and 10 positions of the anthracene should exchange more readily than the others, and the D_2SO_4 exchange produced polydeuterated anthracene, a weaker acid was sought. Para-toluenesulfonic acid was chosen because of its higher pKa and its solubility in organic solvents. The acid was prepared by adding D_2O to a mixture of anthracene and p-toluenesulfonyl chloride in benzene. The exchange occurred rapdily in refluxing

benzene after an induction period of up to 48 hours. This indicated that the hydrolysis of the acid chloride was rate limiting and probably auto-catalytic. The method was satisfactory, but it would probably be more convenient to hydrolyze the sulfonyl chloride in a separate step. The product was isolated by stirring the mixture with saturated aqueous bicarbonate overnight and extracting with benzene. The deuterated product contained 85% anthracene-9,10-d_2, 7% anthracene-d_3, and 7% anthracene-9-d (mole %). The reduction of 9,10-dibromoanthracene with zinc and deuterated acetic acid (15) might also have given us as good or better deuterium incorporation, but this method was not attempted by us, as the acid exchange method provided sufficient deuterium incorporation.

Of the methods available for preparing the other anthracene derivatives, the butadiene-quinone condensation method was chosen because all of the reactions involved had been previously reported with reasonable yields. We could also thus avoid the difficulty reported with the Grignard reactions. All of the deuterated 1,3-butadienes were prepared as reported in the literature, except 1,3-butadiene-2,3-d_2 which was prepared by base catalyzed exchange of perdeutero-3-sulfolene with H_2O, followed by pyrolysis (Figure VI).

1,3-butadiene-1,1,4,4-d_4 was prepared by the method of Cope et al (30). The method involved stirring a solution of potassium carbonate in D_2O and dioxane for 48 hours. After equilibrium, the solvent was removed by freeze drying, fresh D_2O and K_2CO_3 were added, and the solution stirred again for 48 hours. The procedure was repeated seven times by Cope et al, but we found it necessary to repeat the procedure nine times for complete deuteration in one of our runs. Removal of the solvent was faster by heating the solution on a warm water bath under reduced pressure in a rotary evaporator. However, if the water was too hot (near boiling), the sulfolene partially decomposed to some insoluble polymer. The 3-sulfolene-2,2,5,5-d_4 was converted to 1,3-butadiene-1,1,4,4-d_4 and SO_2 by heating for 15 hours in a round-bottomed flask fitted with a nitrogen inlet and connected in series through two gas-absorption traps (containing aqueous NaOH to absorb the SO_2) and a drying tube to a Dry Ice trap. As nitrogen was passed slowly through the apparatus, the product collected in the trap. The reaction went cleanly with only a small brown film remaining in the r.b. flask with the K_2CO_3.

1,3-butadiene-d_6 was prepared by the method of Craig and Fowler (21). Zinc dust and anhydrous dioxane were placed in a round-bottomed flask fitted with a nitrogen

inlet, dropping funnel, condenser, and stirrer. The condenser was connected through a drying tube to a Dry Ice trap. After flushing with nitrogen, NaI, anhydrous CuCl, and D_2O were added. The mixture was refluxed with stirring, and hexachlorobutadiene was added through the dropping funnel over one hour. Nitrogen was passed slowly through the system and the product collected in the Dry Ice trap. An NMR spectrum showed that some dioxane also was collected with the product, but it did not seem to affect the results of the next reaction. Cope et al carried out the addition of the hexachlorobutadiene over a period of five hours in two stages, but this procedure did not improve our yield.

1.3-butadiene-2,3-d_2 was prepared in two steps. 3-sulfolene-d_6 was first prepared by a method similar to that of the Grummitt et al (31). 1,3-butadiene-d_6 was heated in a sealed thick walled glass tube with SO_2 and a small amount of hydroquinone. The product was then exchanged with H_2O in the same manner that the exchange of 3-sulfolene-H_6 with D_2O was carried out.

The butadiene-benzoquinone di-adducts were prepared as by Alder and Stein (28), by heating the reactants in a sealed evacuated thick-walled glass tube with benzene solvent at 120°C for 24 hours. The yields were near 100% when a 2 to 1 excess of butadiene was used, but the yield dropped when the mole ratio of butadiene to benzoquinone was less than 4 to 1.

The butadiene-naphthoquinone adducts were prepared as by Diels and Alder (27) by heating a 1 to 1 mole ratio of butadiene and naphthoquinone in a sealed evacuated thick-walled glass tube with ethanol as solvent at 100°C for 3 hours. The yields were from 90 to 100% except in the case of the 1,3-butadiene-$_{1,1,4,4-d_4}$ reaction. In this case, the sealed tube broke in the oven before the reaction was completed, leaving some starting material with the product. This accounts in part for the low yield of anthracene-1,4-d_2 (2) obtained.

The butadiene-benzoquinone di-adducts were oxidized to anthraquinone by the method of Alder and Stein (28). The adducts were refluxed in 5% ethanolic KOH with a stream of air passing through the solution for 1 hour. The product crystallized out of solution. The yields were nearly quantitative.

The butadiene-naphthoquinone adducts were oxidized by the same method, with 100% yield for the anthraquinone-1,2,3,4-d_4 reaction and 72% for the anthraquinone-2,3-d_2 reaction. The yield in the anthraquinone-1,4-d_2 reaction was not recorded, because of the presence of impurities in the starting material. Diels and Alder (27) used chromium trioxide in acetic acid to oxidize the butadiene-naphthoquinone adduct.

The anthraquinones were reduced to anthracene by the

method of Coffey and Boyd (32), by refluxing the compound in aluminum tricyclohexyloxide solution in cyclohexanol for 48 hours. The solution was poured into water, insoluble material was filtered off and extracted with hot benzene. The benzene and water were separated and the water extracted with benzene. The benzene extracts and soltuion were combined and evaporated. A considerable amount of cyclohexanol still present was removed as an azeotrope with water and benzene. The anthracene was chromatographed on alumina and recrystallized five times from chloroform to remove the last traces of cyclohexanol or other oils present. This extensive purification is largely responsible for the minimal yields obtained for the deuterated anthracenes.

The low-voltage mass spectra of the deuterated anthracenes as compared to those of the deuterated butadienes (Tables I and II) show that some of the deuterium label has been lost along the reaction pathway for compounds 4 and 5. This most likely occurred to the greatest extent in the base-catalyzed air oxidation of the butadiene-quinone adducts as shown in Figure VII. Another oxidation method would possibly eliminate this problem, but no other method was attempted.

The mass spectral data also indicate that some enhancement of deuterium incorporation in compounds 2 and 3

Anthracene	Isotopic Purity (mole %) *		
9,10-d_2 (1)	[a] 13.6 d_1	88.0 d_2	
	[b] 7.2 d_1	85 d_2	7.4 d_3
1,4-d_2 (2)	5.2 d_0	3.6 d_1	91 d_2
1,4,5,8-d_4 (3)	1.1 d_2	3.6 d_3	95 d_4
2,3-d_2 (4)	4.4 d_0	9.5 d_1	86 d_2
2,3,6,7-d_4 (5)	7.4 d_2	16.1 d_3	76 d_4
1,2,3,4-d_4 (6)	4.0 d_0	6.7 d_3	89 d_4

Table I. Isotopic composition of deuterated anthracenes synthesized.

* Values are precise to only $\pm$ 2%.

a. Method a; see Experimental

b. Method b; see Experimental

Compound	Isotopic Purity (mole %) *	
1,3-butadiene-d_6	12.8 d_5	87 d_6
3-sulfolene-d_6	11.0 d_5	89 d_4
3-sulfolene-3,4-d_2	4.0 d_1	96 d_2
3-sulfolene-2,2,5,5-d_4	11.0 d_3	89 d_4

Table II. Isotopic composition of deuterated sulfolenes synthesized.

* Values are precise to only $\pm$ 2%.

has occurred. This could be explained by the fact that in the butadiene-quinone adducts, protons in the 1,4,5 and 8 positions would be more readily removed than deuterons in these positions.

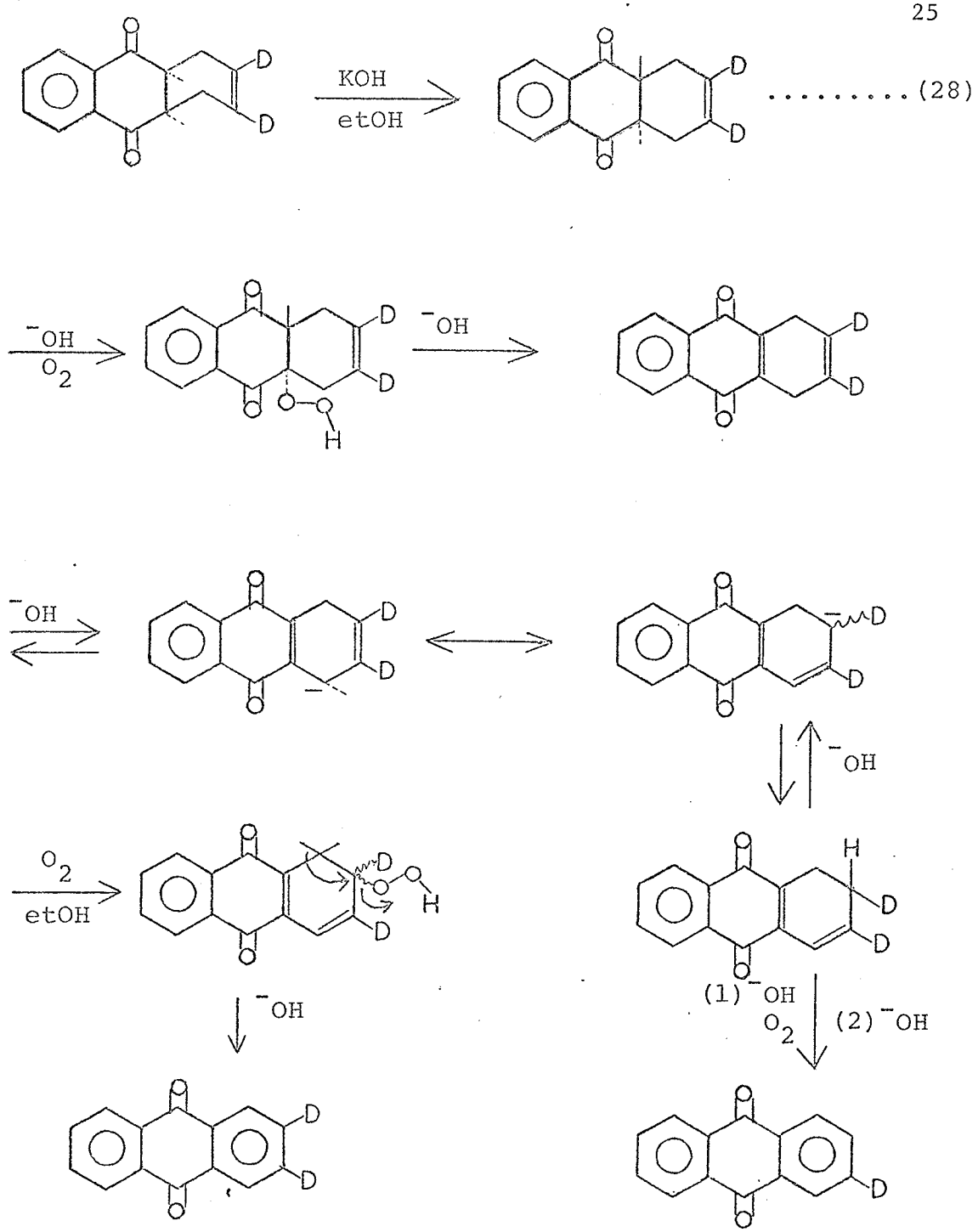


Figure VII. Possible mechanism for base catalyzed air oxidation of butadiene-quinone adducts.

EXPERIMENTAL

Mass spectra were recorded on a Finnigan 1015 mass spectrometer at an ionization energy of 8 eV. Mass ratios were calculated from peak heights and are precise only to $\pm$ 2%. NMR spectra were recorded on a Jeol C-60HL spectrometer and chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 337 Grating Intrared Spectrophotometer. Carbon disulfide was the solvent unless otherwise specified.

Anthracene-9,10,-d_2 (1)

(a) Butyl lithium (0.01 moles in 3 ml. benzene) was added to a solution of 9,10-dibromoanthracene (1.00 g., 0.003 moles) in dry reagent benzene (35 ml.) under nitrogen.

After refluxing 40 minutes and cooling, D_2O (2 ml.) was added, and the solution stirred 5 minutes. The solvent was removed and the residue dissolved in CCl_4. The solution was washed with water, dried ($MgSO_4$), and the solvent evaporated, leaving yellow oily crystals. Chromatography on alumina with pet ether, followed by recrystallization from chloroform gave blue fluorescent plates (50 mg., 9%).

Mass spectrum: m/e (relative intensity) 179(4.9), 180(32), 181(5.0).

(b) Anthracene (0.78 g., Baker sensitizer grade) was dissolved in refluxing benzene (100 ml.) containing p-

toluenesulfonyl chloride (10 g.) and D_2O (2 ml.). Progress of the exchange reaction was followed by mass spectrometry. After 30 hours, the reaction mixture was diluted with benzene (100 ml.) and extracted with aqueous sodium bicarbonate (5%). The benzene fraction was evaporated to dryness and the residue heated on a steam bath for 15 hours with 100 ml. of saturated aqueous bicarbonate. Extraction with $CHCl_3$, drying ($MgSO_4$), and evaporation yielded the crude anthracene-9,10-d_2. This was recrystallized from $CHCl_3$, with treatment with charcoal, to yield blue fluorescent crystals.

Mass spectrum: m/e (relative intensity) 179 (3.5), 180 (42), 181 (10.1). NMR 7.35 (m, 4H), 7.86 (m, 4H).

3-Sulfolene-2,2,5,5-d_4

The method of Cope et al (30) was used with slight modification. 3-Sulfolene (10.0 g.), potassium carbonate (0.11 g.), D_2O (10 g.), and anhydrous dioxane (10 ml.) were stirred at room temperature for 48 hours. The solvents were removed in vacuo at room temperature, fresh D_2O and dioxane added, and the solution again stirred 48 hours. This procedure was repeated seven times and the residue was dried at room temperature under high vacuum. The product was used in the next step without purification.

Mass spectrum: m/e (relative intensity) 57 (3.9), 58 (31.9), 59 (1.8).

1,3-Butadiene-1,1,4,4-d_4

The dried sulfolene-d_4 sample from above was placed in a round-bottomed flask fitted with a nitrogen inlet and connected in series through two gas absorption traps (each containing 25 ml. of 20% aqueous NaOH) and a drying tube (Drierite) to a Dry Ice trap. Nitrogen gas was slowly passed through the system and the sample heated to 130-160°C for 1.5 hours. Five milliliters (79%) of butadiene was collected.

1,3-Butadiene-d_6

The method of Craig and Fowler (21) was used with slight modification. Zinc dust (98 g.) and anhydrous dioxane (114 g.) were placed in a 500 ml. round-bottomed flask fitted with a nitrogen inlet, dropping funnel, condenser, and stirrer. The condenser was connected to a Dry Ice trap. After flushing with nitrogen, NaI (0.8 g.), anhydrous CuCl (4.8 g.) and D_2O (26.4 g.) were added. The mixture was refluxed with stirring and hexchlorobutadiene (52 g.) was added over 1 hour. The yield of crude product was 7.25 ml. (44%).

Mass spectrum: m/e (relative intensity) 59(8.7), 60(59.9), 61(3.1).

3-Sulfolene-d_6

The method of Grummitt et al (31) was used with slight modification. 1,3-Butadiene-d_6 (12 ml.), sulfur dioxide (13.5 ml.), and hydroquinone (0.10 g.) were sealed in a thick-walled glass tube after evacuation at -79°C to 10^{-2} mm Hg. The mixture was heated at 100°C for 12 hours. The crude reaction mixture was dissolved in water and filtered. Evaporation of the water in vacuo and recrystallization from methanol gave 15.8 g. of yellowish-white crystals (84%).

Mass spectrum: m/e (relative intensity) 59(11.0), 60(89.2), 61(4.2).

3-Sulfolene-3,4-d_2

The perdeutero-3-sulfolene (7.12 g.) was treated with H_2O in a manner analogous to the treatment of perhydro-3-sulfolene with D_2O (described above) yielding 6.0 g. of the 3-sulfolene-3,4-d_2 (87%) (some insoluble material formed during the exchange and was filtered off).

Mass spectrum: m/e (relative intensity) 55(2.8), 56(70.0), 57(3.9).

1,3-Butadiene-2,3-d_2

The 3-sulfolene-3,4-d_2 was pyrolyzed as described previously (for 3-sulfolene-2,2,5,5-d_4) to yield 2.2 ml. of

1,3-butadiene-2,3-d_2 (59%).

1,3-Butadiene-1,1,4,4-d_4-p-benzoquinone Adduct

The procedure was similar to that of Alder and Stein ((28). 1,3-Butadiene-1,1,4,4-d_4 (2.0 g.) was distilled into a thick-walled glass tube containing p-benzoquinone (1.0 g.) and benzene (2 ml.). The tube was degassed by three freeze-thaw cycles with evacuation to 10^{-2} mm. Hg, then sealed and heated at 120°C for 24 hours. After cooling the product separated as white crystals and, after evaporation of the benzene, was used without further purification. Yield was 2.0 g. (100%).

Anthraquinone-1,4,5,8-d_4

The anthraquinone was prepared from the octahydroanthraquinone using the method of Alder and Stein (28). The adduct from above (2.0 g.) was refluxed in 5% ethanolic KOH (50 ml.) with a stream of air passing through the mixture for 1 hour. The mixture was diluted with water, neutralized with 1 N HCl, and the quinone extracted with $CHCl_3$. The combined extracts were dried ($MgSO_4$) and evaporated to dryness to yield 1.89 g. (98%) which was used without further purification.

Anthracene-1,4,5,8-d_4 (3)

Anthraquinone-1,4,5,8-d_4 from above (1.0 g.), aluminum tricyclohexyloxide solution (10 ml., see preparation below), and cyclohexanol (5 ml.) were refluxed 48 hours. The solution was poured into water (50 ml.), benzene added (50 ml.), and the mixture filtered, washing the residue well with hot benzene. The benzene and water were separated and the water extracted with benzene. The benzene solutions and extracts were combined and evaporated in vacuo. The residual cyclohexanol was removed as an azeotrope with water and benzene. The antracene was chromatographed on alumina (Woelm, GrI; eluant benzene) and recrystallized five times from chloroform. Yield of blue fluorescent crystals, 0.173 g. (21%).

Mass spectrum: m/e (relative intensity) 181 (2.9), 182(91.8), 183(15.3).

NMR: 7.34 (s, 4H), 8.24 (s, 2H).

Aluminum Tricyclohexyloxide Solution

Aluminum wire (5 g.), cyclohexanol (100 ml., distilled from CaO), mercuric chloride (25 mg.), and CCl_4 (1 ml.) were refluxed overnight. The solution was used without further treatment.

1,3-Butadiene-1,1,4,4-d_4-1,4-naphthoquinone Adduct

1,3-Butadiene-1,1,4,4-d_4 (5 ml.), 1,4-naphthoquinone (11.0 g.), and ethanol (5 ml.) were heated in an evacuated, sealed heavy-walled glass tube at 100°C for 3 hours. The solvent was removed in vacuo and the product used without further purification.

Anthraquinone-1,4-d_2

The crude adduct from above (6.2 g.) was oxidized in 5% ethanolic KOH (ca. 50 ml.) with air as previously described to yield 2.55 g. of crude anthraquinone-1,4-d_2.

Anthracene-1,4-d_2 (2)

The crude anthraquinone-1,4-d_2 (2.0 g.) was reduced as previously described with aluminum tricyclohexyl oxide (20 ml. of prepared solution), and 10 ml. of cyclohexanol to give, after purification, 84.5 mg. of anthracene-1,4-d_2 (5%).

Mass spectrum: m/e (relative intensity) 178(4.5), 179(3.8), 180(80.0), 181(13.0).

NMR: 7.35 (m, 4H), 7.86 (m, 2H) 8.23 (s, 2H).

1,3-Butadiene-2,3-d_2-p-benzoquinone Adduct

1,3-Butadiene-2,3-d_2 (2.2 ml.), p-benzoquinone (0.65 g.), and benzene (2.5 ml.) were sealed in an evacuated thick-walled tube and heated to 120°C for 24 hours. The slightly yellow crystalline product (1.17 g., 90%) was used without further purification.

Anthraquinone-2,3,6,7-d_4

The adduct from above (1.17 g.) was air-oxidized in 5% ethanolic KOH (ca. 50 ml.) as previously described to yield 0.67 g. (71%) of crude anthraquinone which was not further purified.

Anthracene-2,3,6,7-d_4 (5)

Anthraquinone-2,3,6,7-d_4 (0.64 g.) was reduced with aluminum tricyclohexyloxide (6.5 ml. of prepared solution) and 3.5 ml. of cyclohexanol as previously described to yield 81 mg. of purified anthracene-2,3,6,7-d_4 (14.5%).

Mass spectrum: m/e (relative intensity) 180(7.4), 181(17.0), 182(72.2), 183(13.8).

NMR: 7.86 (s, 4H), 8.35 (s, 2H).

1,3-Butadiene-2,3-d_2-1,4-naphthaquinone Adduct

The adduct was prepared as described above from

1,3-butadiene-2,3-d_2 (0.42 ml.) and 1,4-naphthoquinone (1.2 g.) in 2 ml. ethanol. The crude product (1.56 g., 97%) was used without further purification.

Anthraquinone-2,3-d_2

The adduct from above (1.56 g.) was air-oxidized in 5% ethanolic KOH (ca. 30 ml.) yielding 1.13 g. (72%) of the anthraquinone after work-up (see above).

Anthracene-2,3-d_2 (4)

The crude anthraquinone-2,3-d_2 (1.13 g.) was reduced with aluminum tricyclohexyloxide (12 ml. of prepared solution) and 6 ml. of cyclohexanol in the previously described manner to yield 0.167 g. of anthracene-2,3-d_2 (17.2%) after purification.

Mass spectrum: m/e (relative intensity) 178(4.0), 179(9.3), 180(80.), 181(14.1).

NMR: 7.32 (m, 2H), 7.86 (m, 4H), 8.25 (s, 2H).

1,3-Butadiene-d_6-1,4-naphthoquinone Adduct

The adduct was prepared, as previously described, from butadiene-d_6 (8 ml.) and 1,4-naphthoquinone in 15 ml. of ethanol. Work-up yielded 14.2 g. (89%) of the crude adduct used without purification.

Anthraquinone-1,2,3,4-d_4

The adduct above (14.2 g.) was air-oxidized in 5% ethanolic KOH (ca. 100 ml.) to yield 13.8 g. (100%) of crude anthraquinone-1,2,3,4-d_4.

Anthracene-1,2,3,4-d_4 (6)

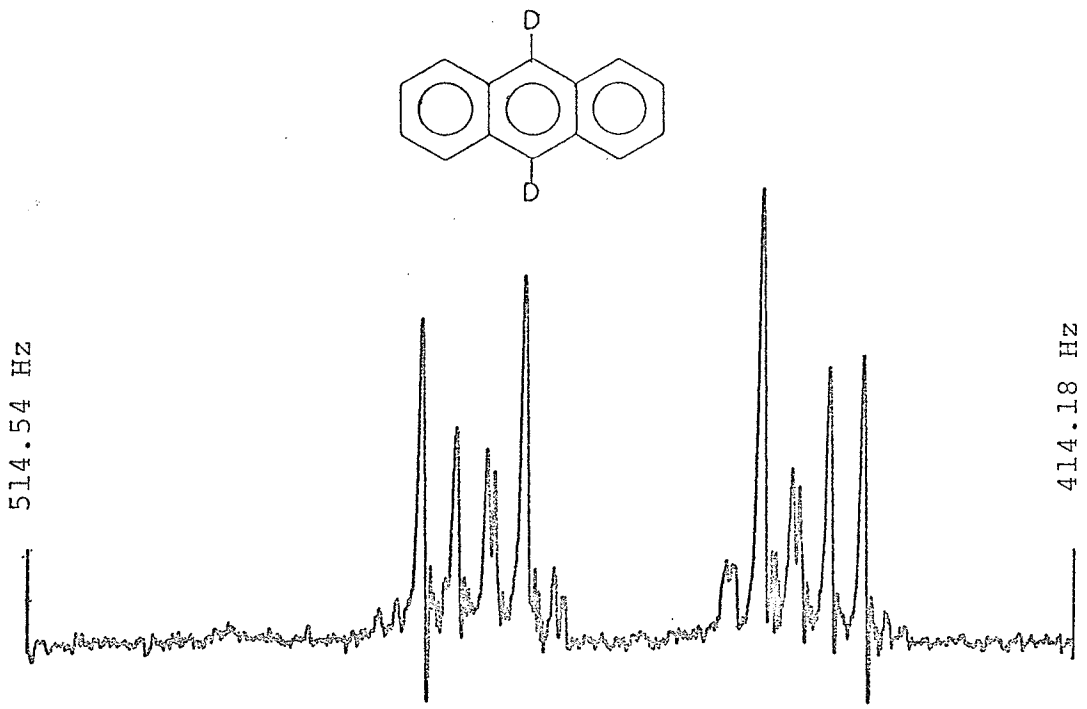
The anthraquinone-1,2,3,4-d_4 (5.0 g.) was reduced with tricyclohexyloxide (50 ml. of the prepared solution) and 25 ml. of cyclohexanol to yield 0.11 g. of purified anthracene-1,2,3,4-d_4 (3%).

Mass spectrum: m/e (relative intensity) 178 (4.8), 181 (8.0), 181 (108), 183 (17.0).

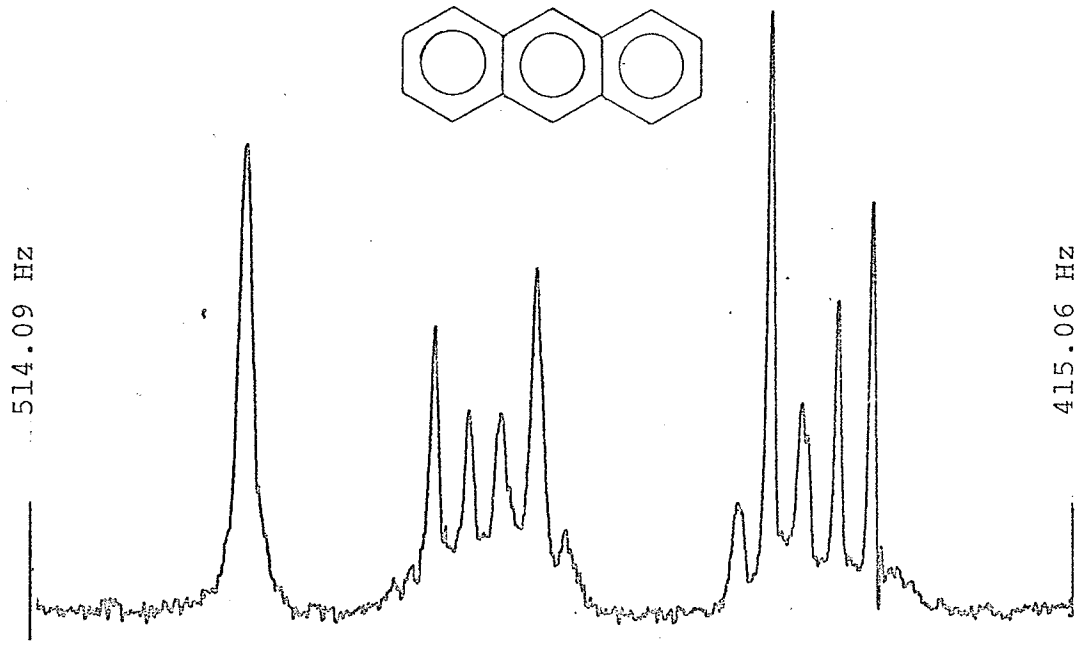
NMR: 7.32 (m, 2H), 7.80 (m, 2H), 8.23 (s, 2H).

NMR SPECTRA

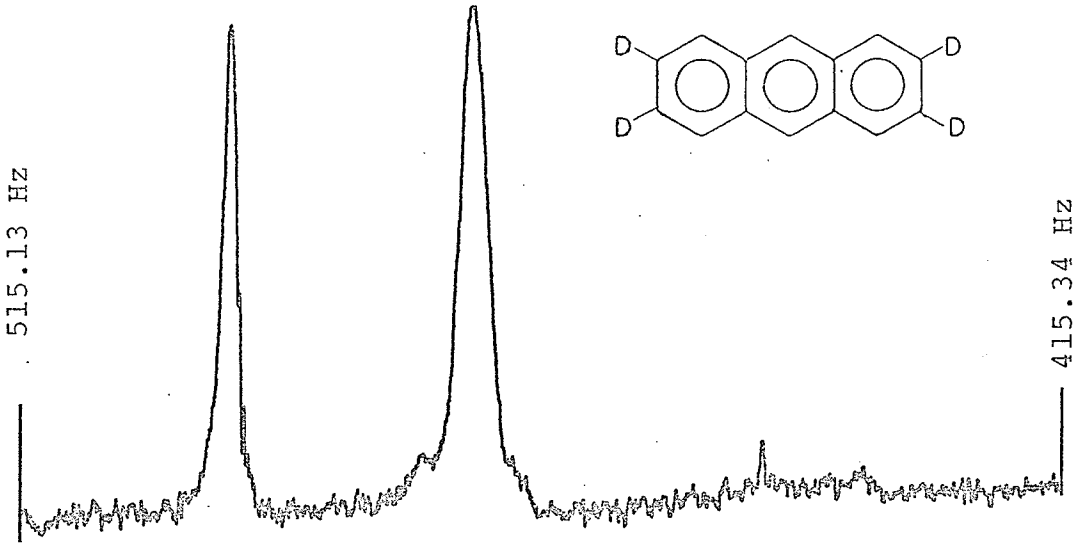
Spectra were recorded on a Jeol C-60HL spectrometer at a sweep rate of 0.54 p.p.m. per minute. Spectra are calibrated in Hertz downfield from tetramethylsilane. Carbon disulphide was the solvent.



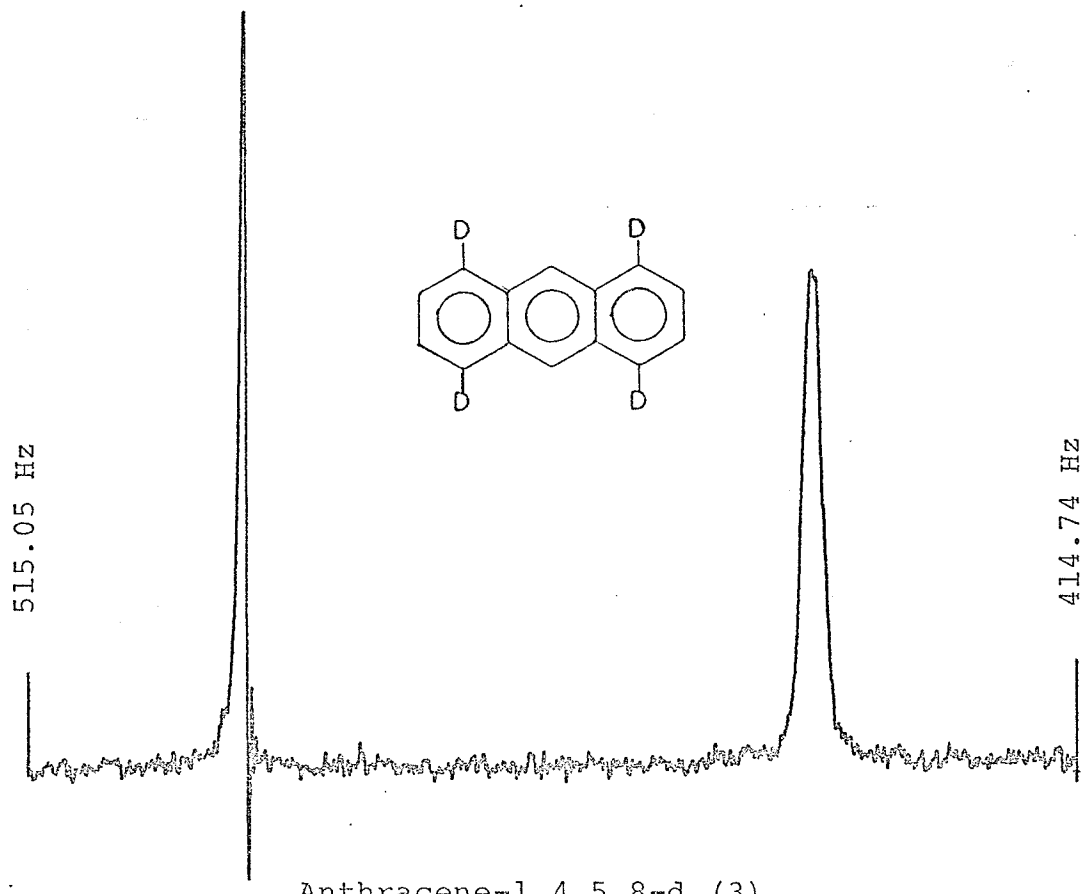
Anthracene-9,10-d_2 (1).



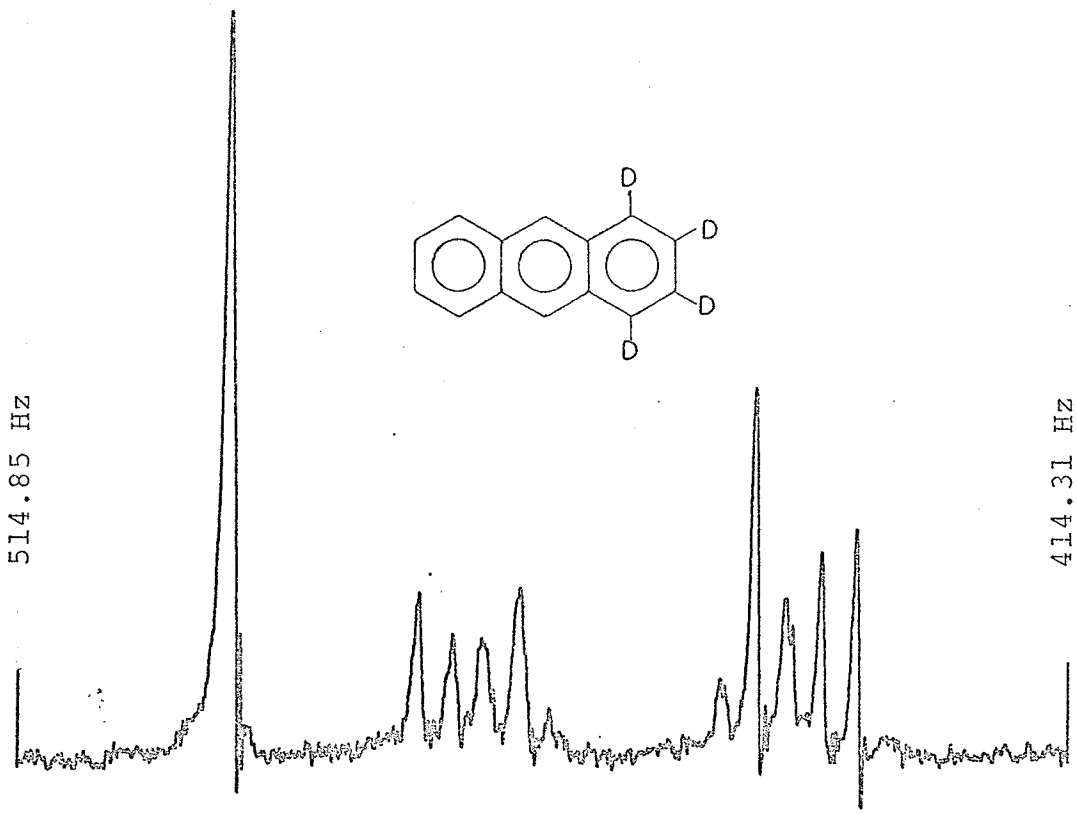
Anthracene-H_{10}



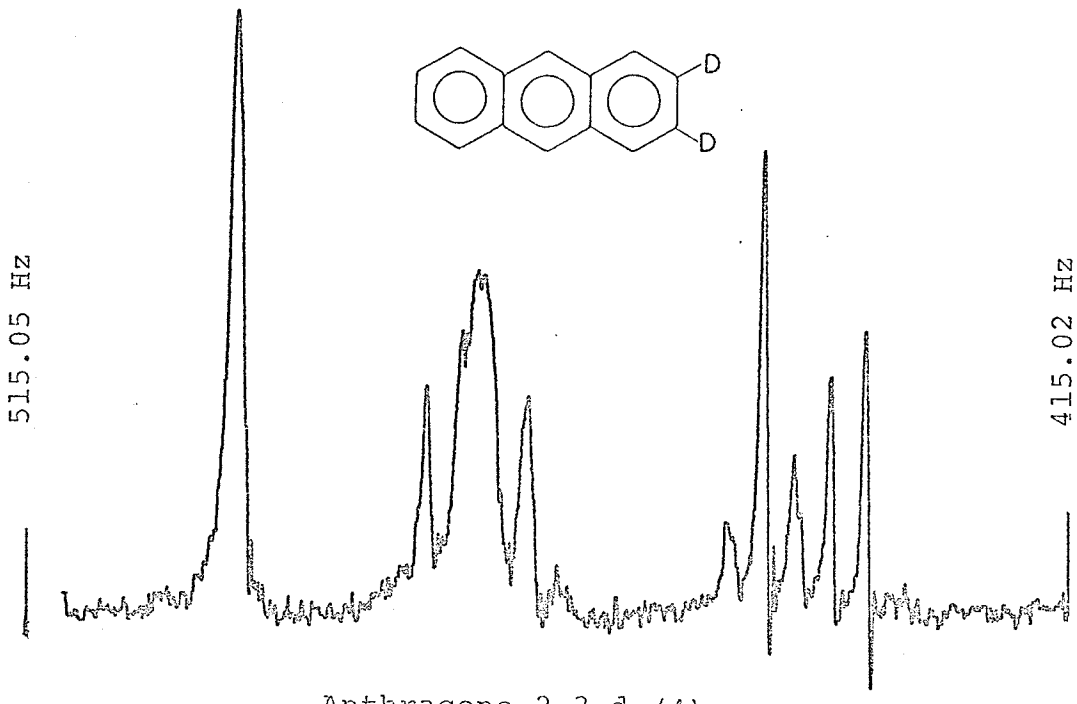
Anthracene-2,3,6,7-d_4 (5).



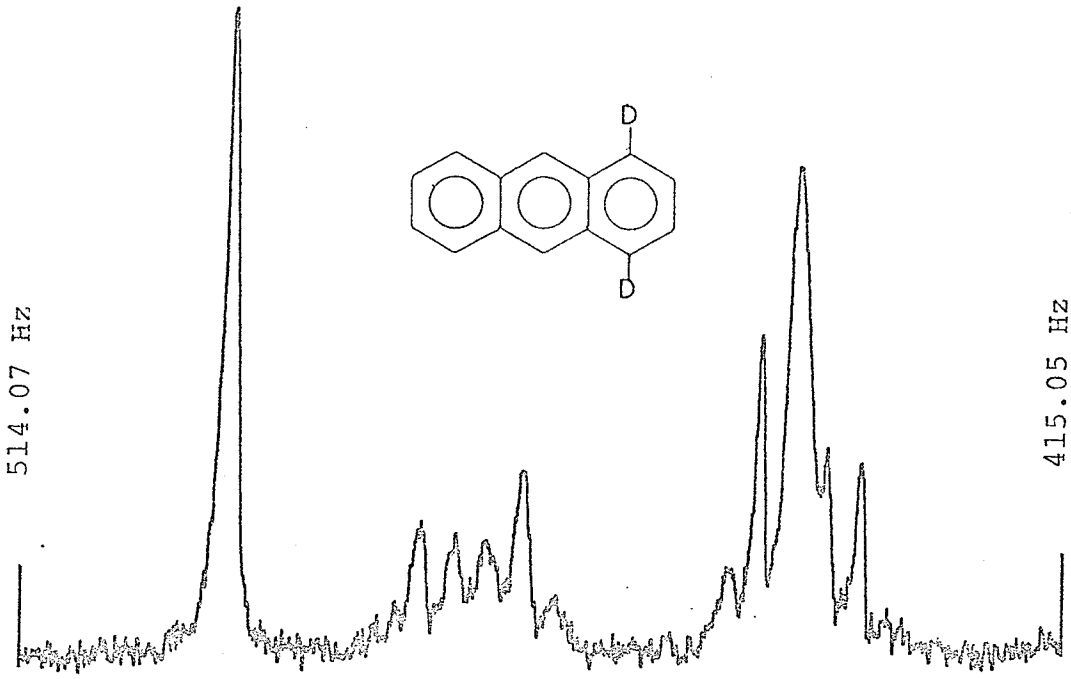
Anthracene-1,4,5,8-d_4 (3).



Anthracene-1,2,3,4-d_4 (6).



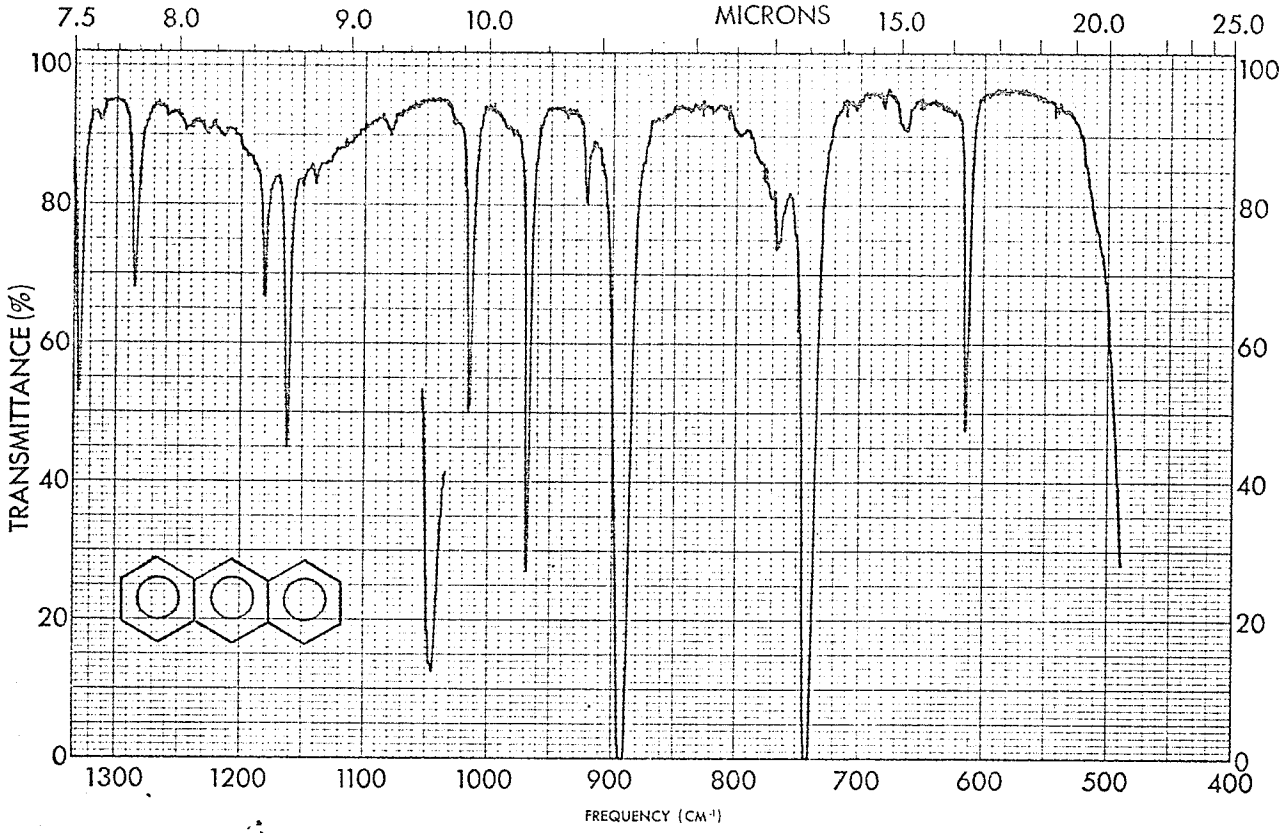
Anthracene-2,3-d_2 (4).

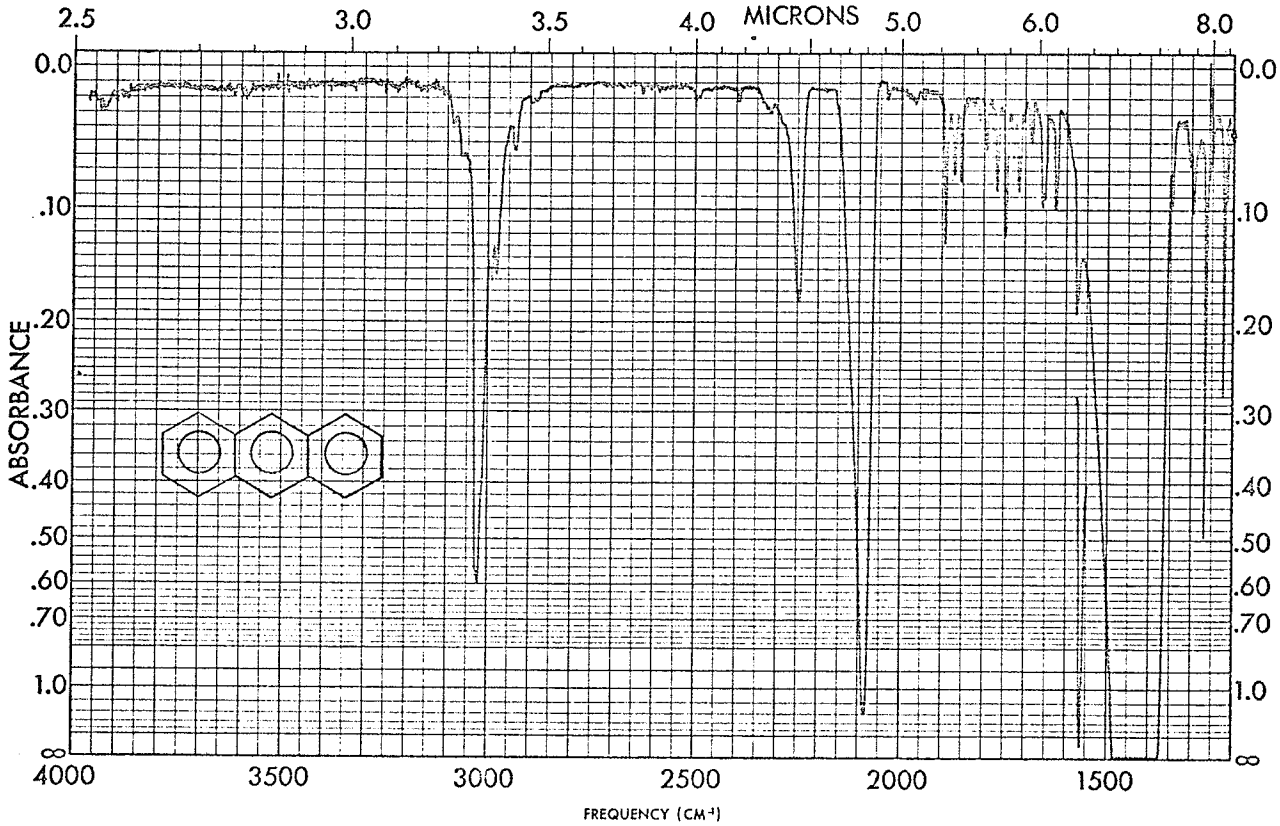


Anthracene-1,4-d_2 (2).

INFRARED SPECTRA

Infrared spectra were recorded on a Perkin-Elmer 337 Grating Infrared Spectrophotometer, using saturated solutions of the anthracenes at room temperature in 0.5 mm. cells.





SAMPLE Anthracene $C_{14}H_{10}$	CURVE NO.	SCAN SPEED FAST	OPERATOR
	CONC. Saturated at room Temp.	SLIT	DATE Aug. 30 '72
ORIGIN	CELL PATH 0.5 mm.	REMARKS	
SOLVENT CS_2	REFERENCE air		

PART NO. 337-1207

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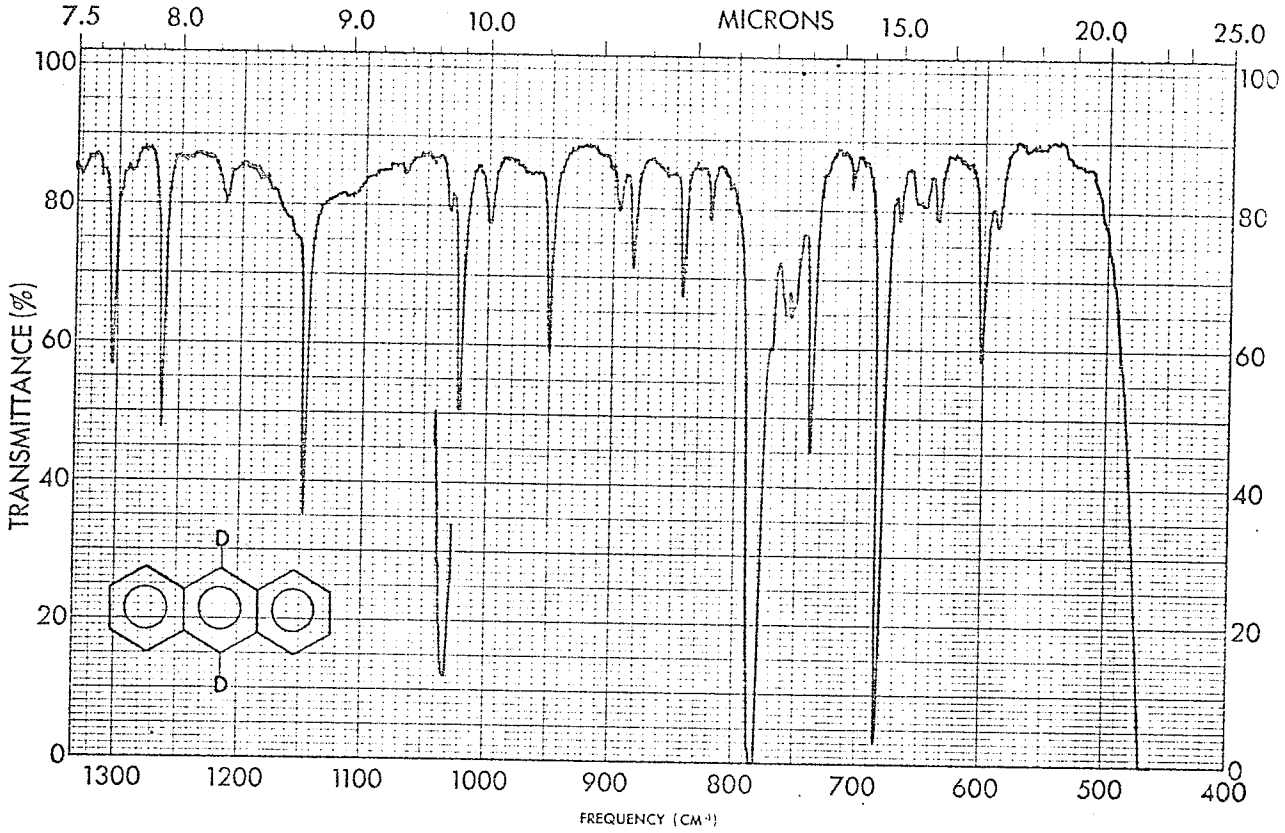

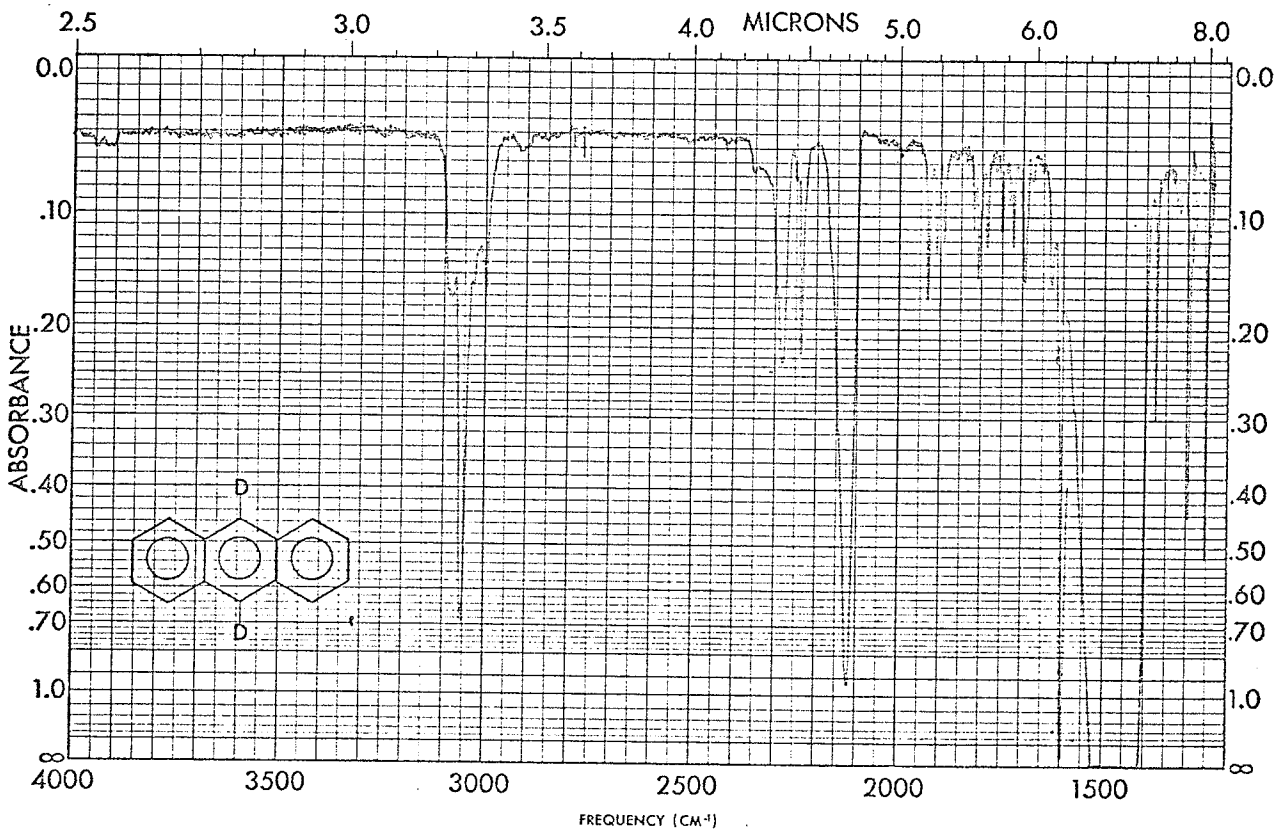

SAMPLE Anthracene-9,10-d_2(1) $C_{14}H_8D_2$	CURVE NO.	SCAN SPEED FAST	OPERATOR
ORIGIN	CONC. saturated at room temp.	SLIT	DATE Aug. 30/72
SOLVENT CS_2	CELL PATH 0.5 mm	REMARKS	
	REFERENCE air		

PART NO. 337-1207

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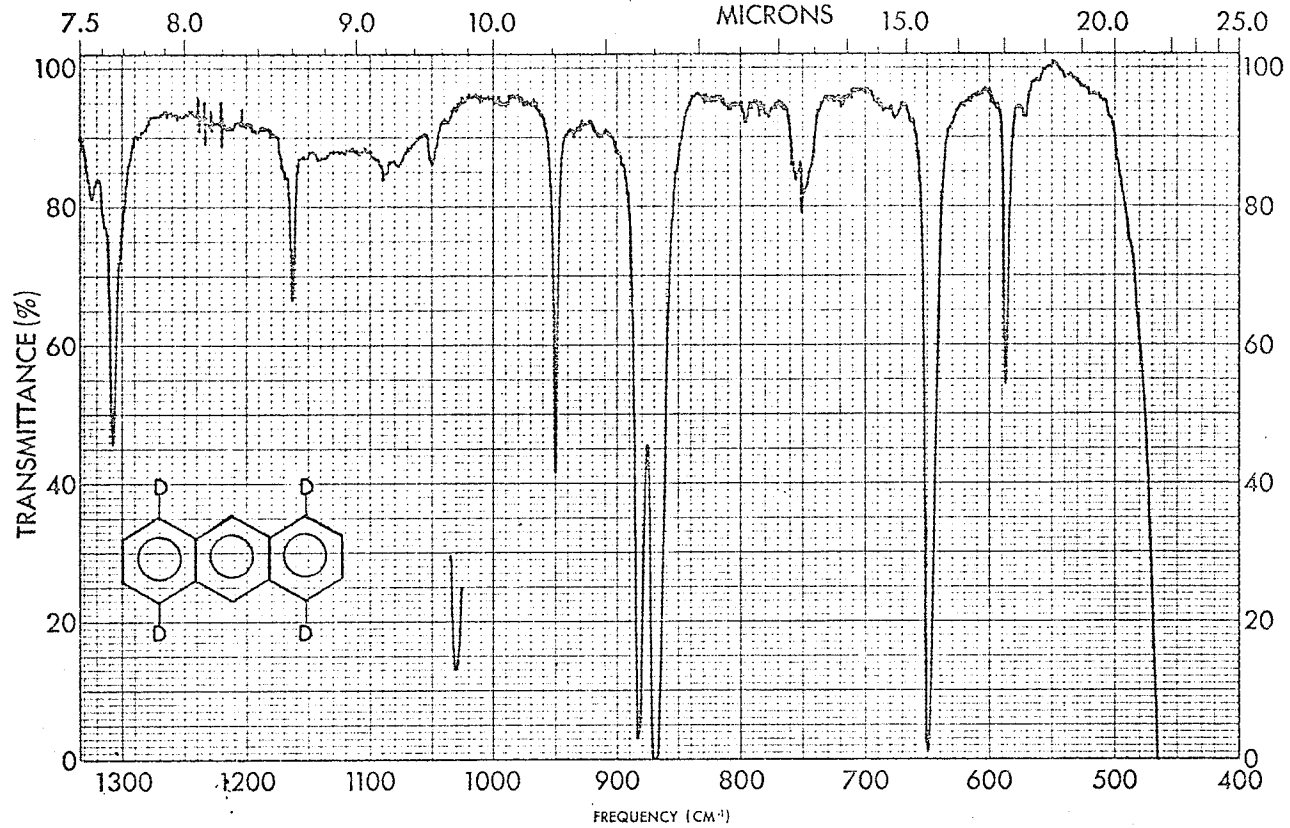

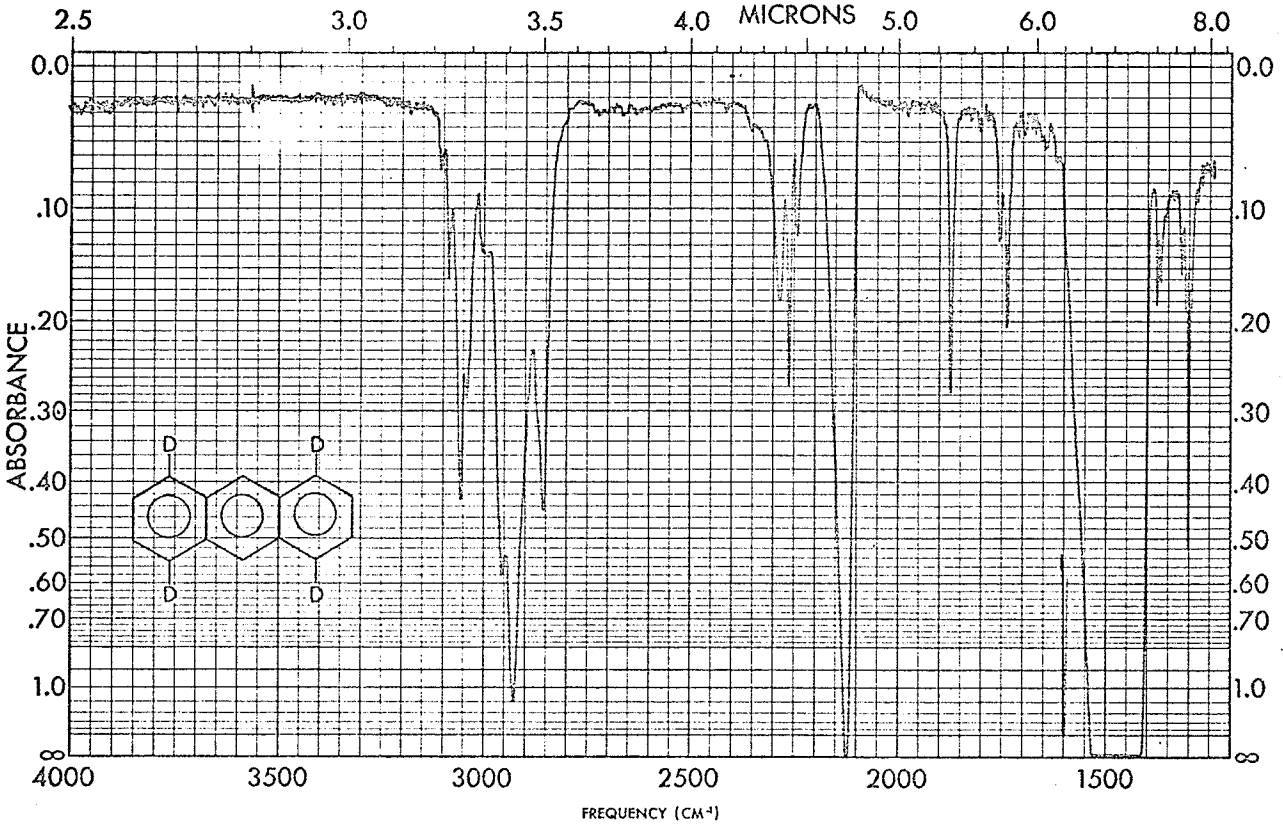

SAMPLE Anthracene-1,4,5,8-d4 $C_{14}H_6D_4$ (I)	CURVE NO.	SCAN SPEED FAST	OPERATOR
ORIGIN	CONC. Saturated at room temp.	SLIT	DATE Aug. 31/72
SOLVENT CS_2	CELL PATH 0.5 mm.	REMARKS	
	REFERENCE air		

PART NO. 337-1207

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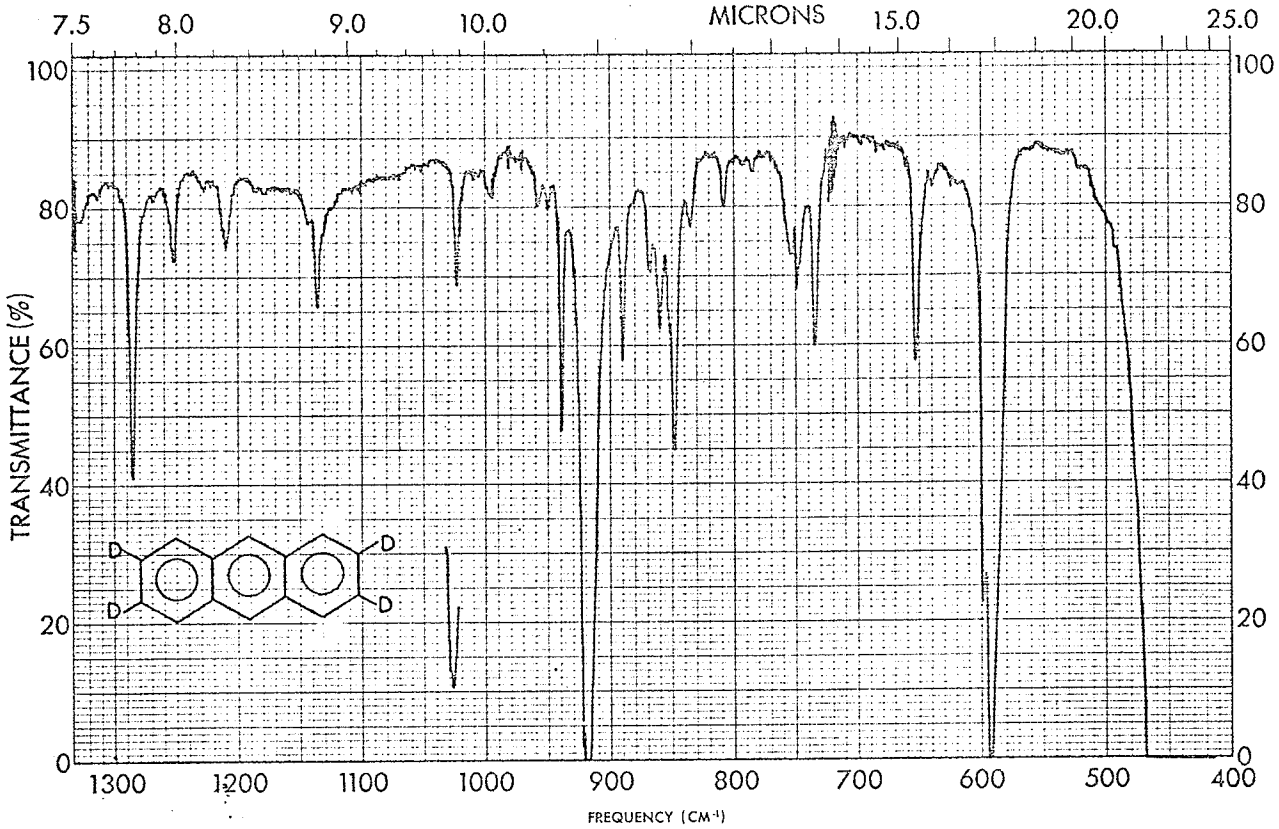

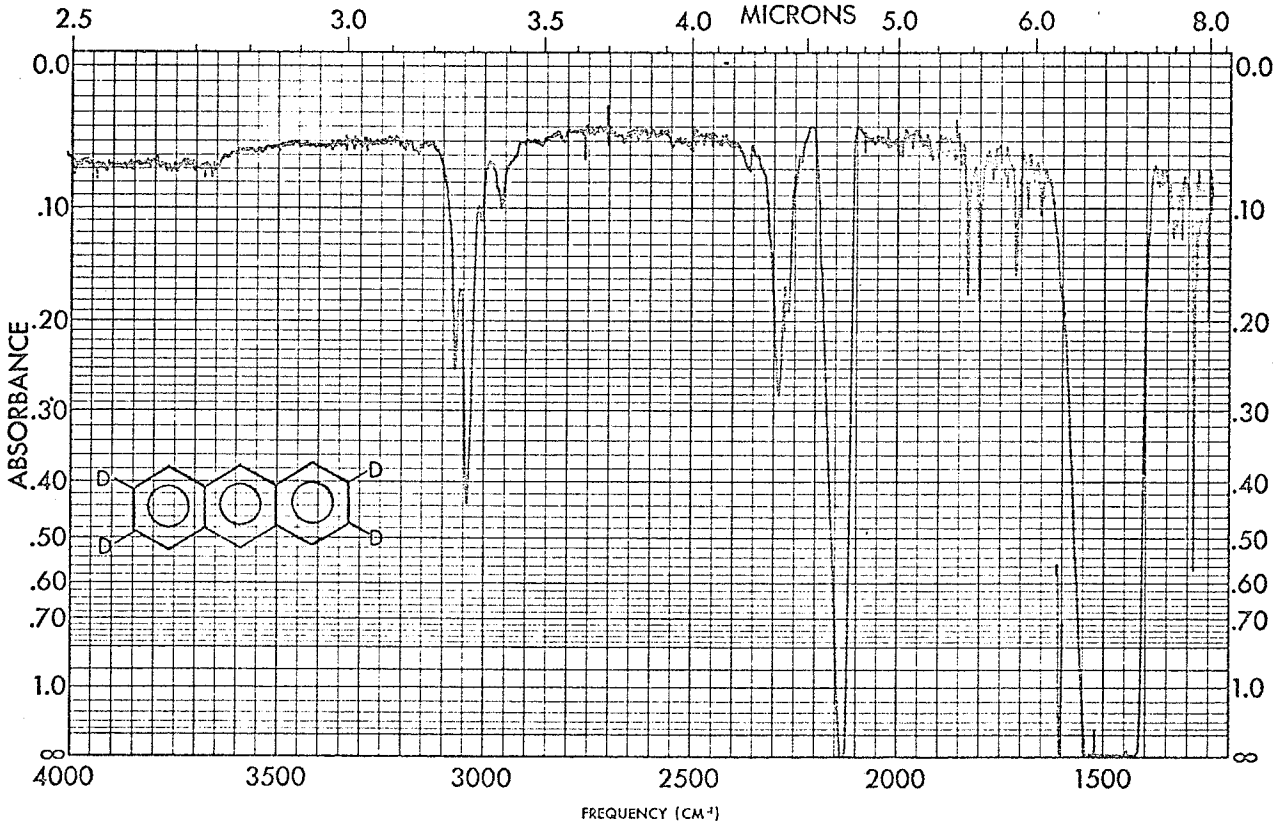

SAMPLE Anthracene-2,3,6,7-d4 C14H6D4 (5)	CURVE NO.	SCAN SPEED FAST	OPERATOR
	CONC. Saturated at room temp.	SLIT	DATE Aug. 31/72
ORIGIN	CELL PATH 0.5 mm.	REMARKS	
SOLVENT CS2	REFERENCE		

PART NO. 337-1207

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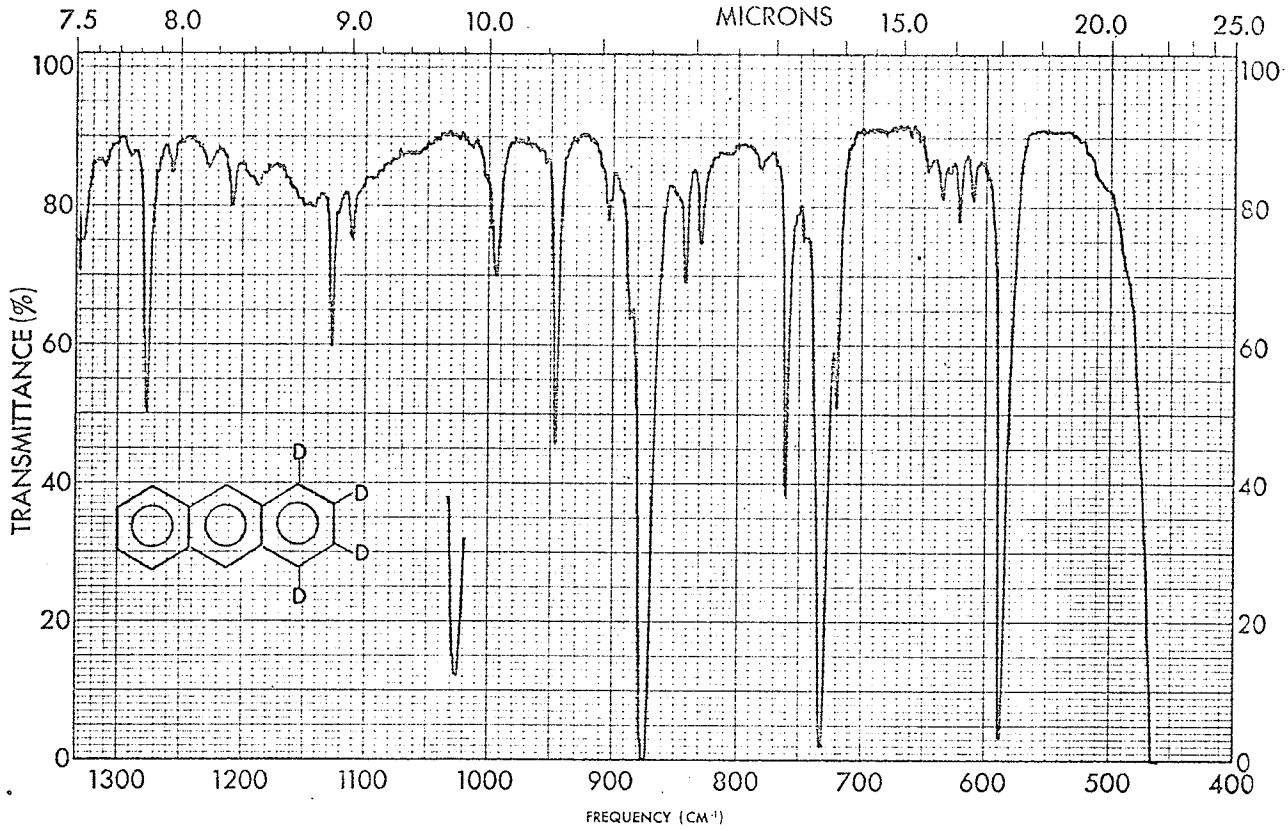

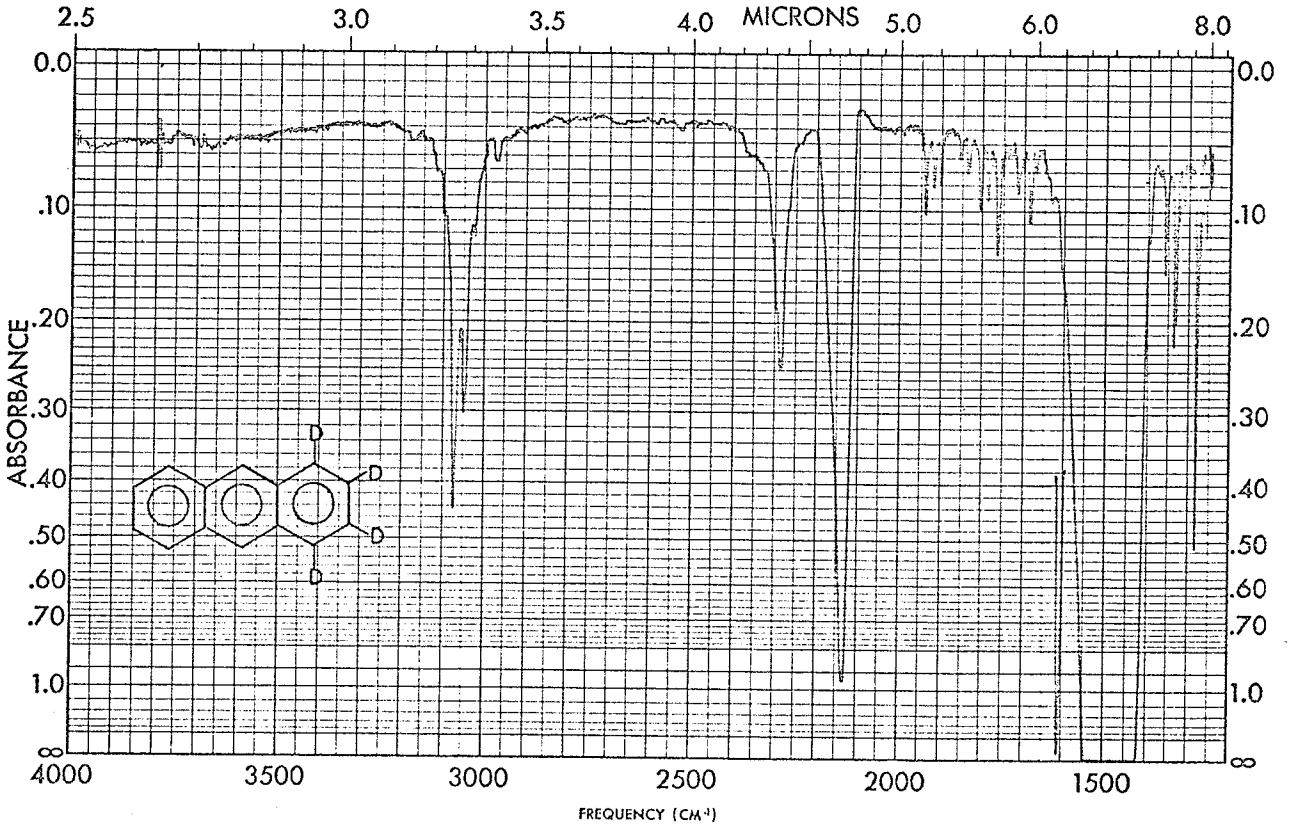

SAMPLE Anthracene-1,2,3,4-d4 $C_{14}H_6D_4$ (6)	CURVE NO.	SCAN SPEED FAST	OPERATOR
ORIGIN	CONC. Saturated at room temp.	SLIT	DATE Aug. 31/72
SOLVENT CS_2	CELL PATH 0.5 mm.	REMARKS	
	REFERENCE air		

PART NO. 337-1207

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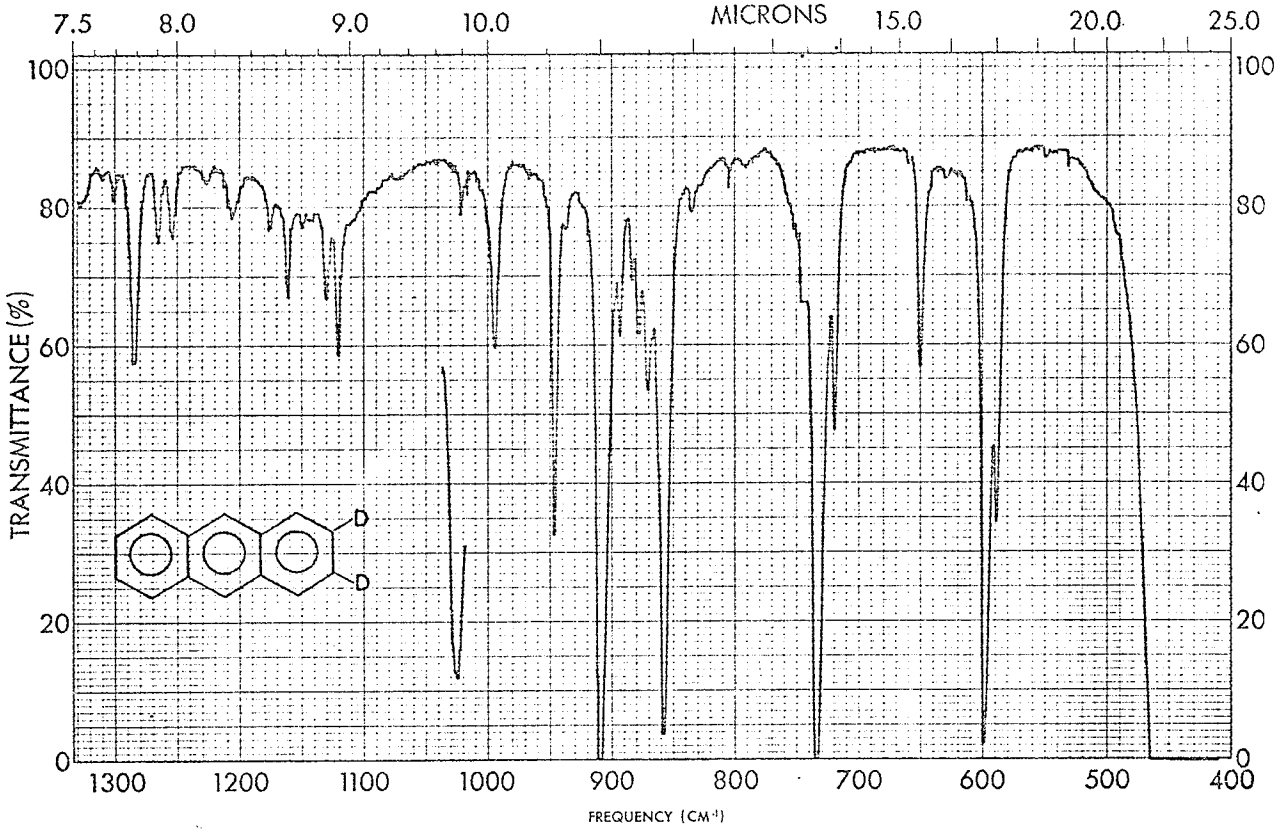

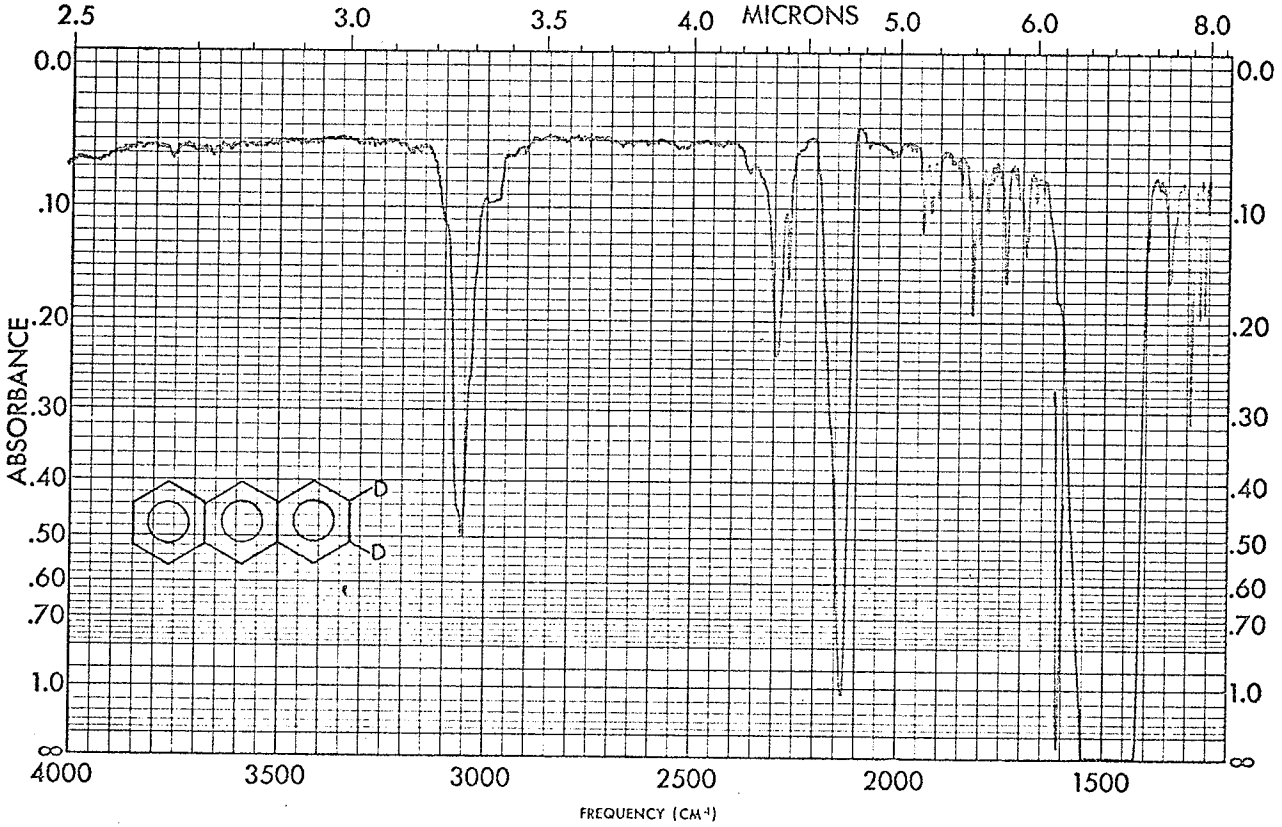

SAMPLE Anthracene-2,3-d_2(4) $C_{14}H_8D_2$	CURVE NO.	SCAN SPEED FAST	OPERATOR
ORIGIN	CONC. Saturated at room temp.	SLIT	DATE Aug. 30 '72
SOLVENT CS_2	CELL PATH 0.5 mm.	REMARKS	
	REFERENCE air		

PART NO. 337-1207

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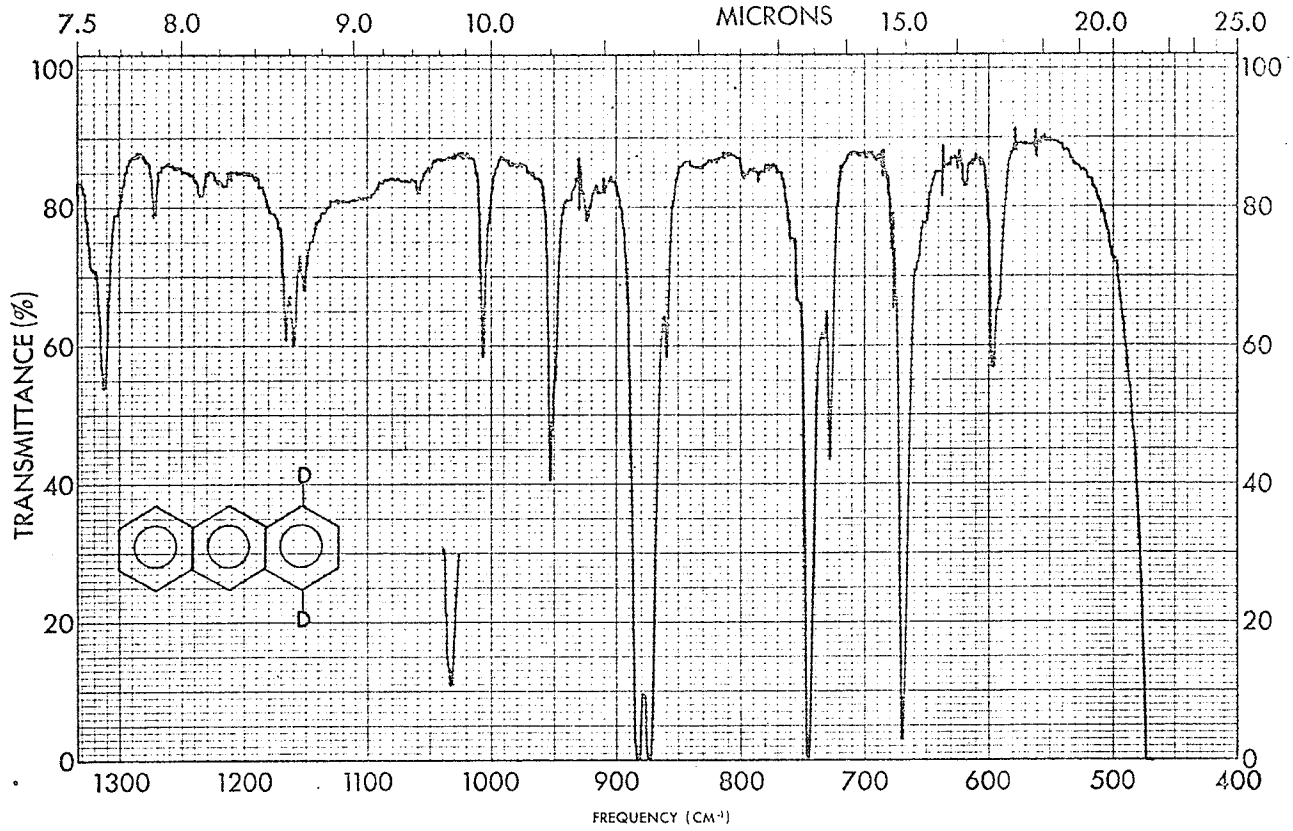

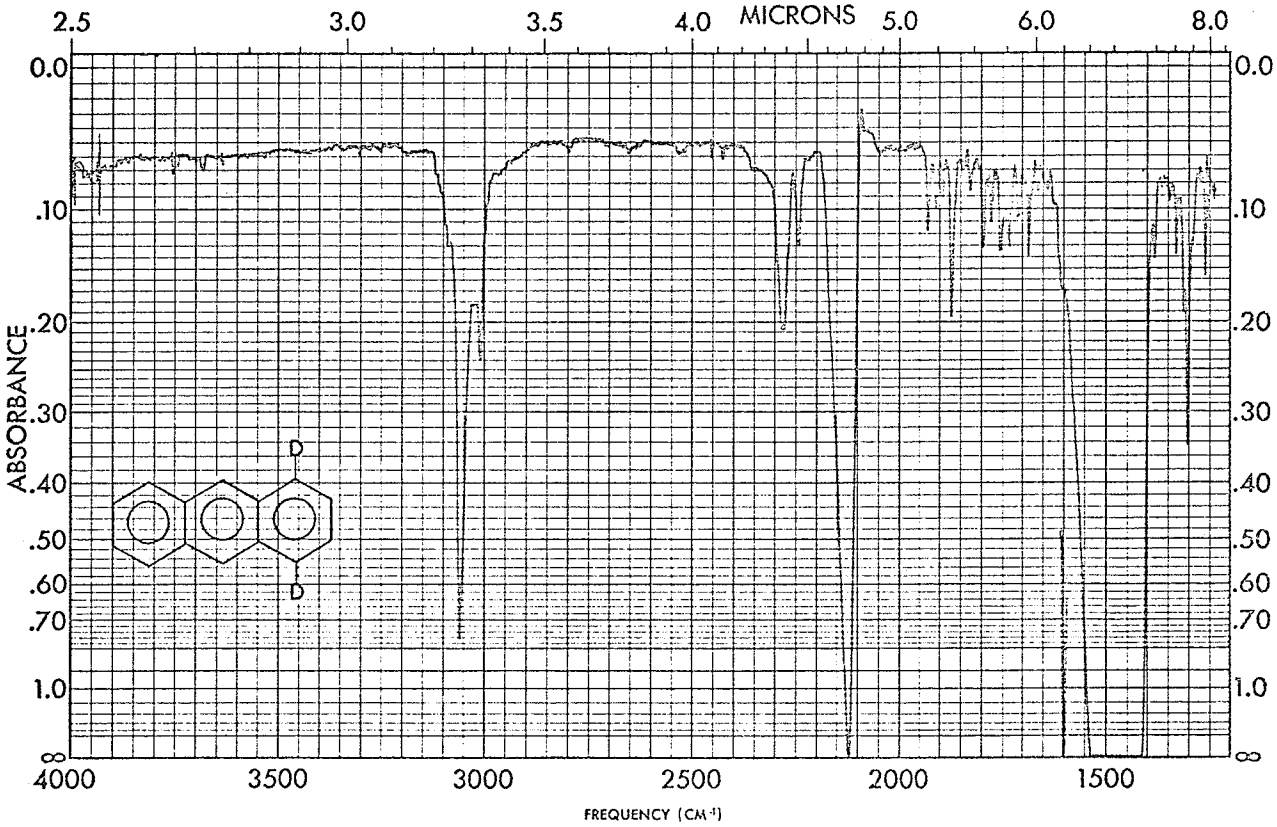

SAMPLE Anthracene-1,4-d_2 (?)	CURVE NO.	SCAN SPEED FAST	OPERATOR
	CONC. Saturated at room temp.	SLIT	DATE Aug. 30/72
ORIGIN	CELL PATH 0.5 mm.	REMARKS	
SOLVENT CS_2	REFERENCE air		

PART NO. 337-1207

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