3,6-Bis(trifluoromethyl)-*s*-tetrazine.[28] *s*-Tetrazine-3,6-dicarboxylic acid (1.8 g, 0.01 mole) was loaded into a section of stainless-steel tubing closed at one end with a cap containing a Teflon ring and connected to a high-pressure valve which carried a metal ball joint. The bomb, of 15–20 ml capacity, was evacuated and sulfur tetrafluoride[29] (6.5 g, 0.06 mole, an excess) was condensed into it at −196°. The bomb was heated at 75° for 10 hr.

After cooling to room temperature the bomb was attached to a vacuum manifold and its contents pumped through three traps in series, the first two at −78° and the last at −196°. The contents of the last trap, which was a mixture of sulfur tetrafluoride, thionyl fluoride, and silicon tetrafluoride, was returned to the bomb, which still contained nonvolatile material. It was further heated at 100° for 8 hr. The contents was fractionated as before and all the material condensed at −78° combined. This mixture was orange in color and obviously contained hydrogen fluoride, as it etched the glass trap upon warming. The mixture was allowed to sublime four times under vacuum through a glass tube packed with sodium fluoride and silica gel. Some material remained adsorbed on the silica gel. The volatile fraction was free of hydrogen fluoride and water as evidenced by its infrared spectrum. The highest peak in its mass spectrum was at *m/e* 218, and the spectrum was completely consistent with that expected for bis(trifluoromethyl)-*s*-tetrazine.

An additional quantity of the tetrazine could be obtained by extraction of the sodium fluoride–silica gel with methylene chloride, concentration of the extract by fractionation of the solvent through a spinning-band column, and subsequent purification by bulb-to-bulb distillation at −30°. The orange, thermochromic compound had prominent infrared absorptions (gas phase) at 1428, 1323, 1207, 1190, 1165, 1148, 1067, 769, and 764 cm^{-1}.

Anal. Calcd for $C_4F_6N_4$: C, 22.02; F, 52.29; N, 25.69. Found: C, 22.35; F, 52.43; N, 24.44.

Acknowledgment. We thank Dr. T. Shannon and Professor F. W. McLafferty for the high-resolution measurements and metastable ion-containing spectra, and Mr. Ronald Kent for help with some of the synthetic aspects of the work. The generosity of the Socony-Mobil Oil Company is acknowledged with gratitude. A preliminary study of 3,6-dichloropyridazine by Mr. Kenneth M. Cohen is gratefully acknowledged.

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(28) This synthesis was carried out as a joint project with Mr. Ronald Kent, University of Pennsylvania.

(29) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, 82, 543 (1960).

Triarylmethyl Radicals. Synthesis and Electron Spin Resonance Studies of Sesquixanthydryl Dimer and Related Compounds[1]

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H. S. Gutowsky, and J. C. Martin

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Abstract: Factors influencing the dissociation of hexaarylethane into triarylmethyl radicals have been illustrated through synthesis and electron spin resonance (esr) studies of two novel triarylmethyl derivatives. Radical II, 2,6,2′,6′,2′′,6′′-hexamethoxytriphenylmethyl, is extremely hindered toward attack at the central carbon atom, reacting only slowly with oxygen. There is no evidence of dimerization, even in the solid state. Evidence for a pronounced angle (∼50°) of twisting of the aryl rings from the plane defined by the central carbon and the three carbons bonded to it is seen in the esr hyperfine interaction with the *para* protons ($a_{para} = 2.26 \pm 0.02$ gauss, compared with 2.77 gauss for the unsubstituted triphenylmethyl). Additional evidence for the larger angle of twist is supplied by the large ^{13}C hfs constant (26 gauss) found in radical II enriched with ^{13}C at the central carbon. The importance of steric interactions in promoting dissociation of hexaarylethanes is reflected in the stability of sesquixanthydryl dimer (III) which is undissociated in the solid and essentially undissociated in solution. Only very weak esr signals could be obtained from solutions of III.

Two principal factors have been postulated to provide the primary driving force for the dissociation of hexaarylethanes to yield free radicals: (a) the resonance stabilization of the radical, and (b) the relief upon dissociation of steric interactions between aryl groups either on the same carbon or on adjacent carbons in the ethane. Estimates[2] of the relative importance of these two factors, based on thermochemical data for the unsubstituted hexaphenylethane, suggest that the resonance effect (50–55 kcal/mole) is about twice as important as the steric effect (17–22 kcal/mole) in promoting the dissociation of this ethane, relative to the dissociation of ethane itself to give two methyl radicals. Many existing data[3] provide qualitative support for the suggested important contributions from each of these effects. The novel free radicals I and II, accessible by reduction of the corresponding carbonium ions,[4] provide extreme cases for the further elucidation of the factors governing the dissociation.

The sesquixanthydryl radical (I) provides a minimum of steric hindrance to dimerization, and the postulated coplanar structure of the radical provides the optimum geometry for delocalization of the odd electron. Radical II, bearing six *o*-methoxy substituents, is expected to have a relatively large angle of twist of the phenyl groups (pitch of the propeller) in its most stable con-

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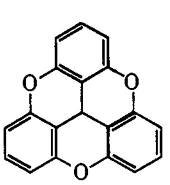
(1) Taken in part from the Ph.D. Theses of M. J. S. and R. G. S., University of Illinois.

(2) H. E. Bent and F. R. Cuthbertson, *J. Am. Chem. Soc.*, **58**, 170 (1936); J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter I; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 18.

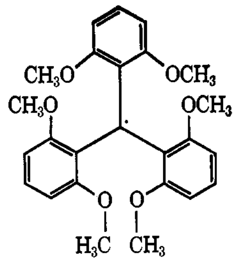
(3) G. Wheland, "Advanced Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1960: (a) pp 763 ff; (b) p 784; (c) p 779.

(4) J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964).

formation, which would reduce the resonance stabilization of the radical. At the same time, we expect a large steric hindrance to dimerization of II because of its extreme steric crowding.



I



II

Experimental Section[5]

Sesquixanthydryl Dimer III. Sesquixanthydrol and sesquixanthydryl chloride were prepared as previously described.[4] The reduction to the dimer was accomplished in several different ways: electrolysis in aqueous solution, treatment of sesquixanthydryl chloride with molecular silver, and irradiation of solutions of sesquixanthydrol in aqueous ethanolic HCl. The most satisfactory preparative procedure involved reduction with chromous chloride. In a typical procedure, sesquixanthydryl chloride dihydrate (2.0 g, 0.0056 mole) was dissolved in 150 ml of glacial acetic acid and 10 ml of concentrated sulfuric acid. A dilute solution of chromous chloride, from passage of a dilute (0.1 *M*) aqueous sulfuric acid solution of chromic chloride through a Jones Reductor,[6] was added slowly to this solution under a nitrogen atmosphere. A yellow solid crystallized from the reaction medium during the addition. The addition was stopped when the mixture took on a permanent blue color, and then 200 ml of water was added. Filtration gave 1.50 g of crude dimer, mp 280–300° dec, essentially insoluble in ethanol, acetone, benzene, chloroform, diglyme, dioxane, tetrahydrofuran, and trifluoroacetic acid. The material was sparingly soluble in boiling methyl benzoate or anisole to give a light green solution from which white crystals were deposited on cooling (mp 300° dec); infrared (KBr pellet): 1623 (s), 1497 (m), 1471 (s), 1273 (s), 1070 (m), 1022 (m), 864 (w), 766 (s), and 660 (s) cm^{-1}. *Anal.* Calcd for $C_{38}H_{18}O_6$: C, 80.00; H, 3.18. Found: C, 79.32; H, 3.40.

The material may be sublimed at 10^{-5} mm to give 10–30% recovery of dimer. The mass spectrum of the material (at 10 ev) gave a strong peak at *m/e* 285, characteristic of the sesquixanthydryl cation. With the normal leak inlet of the Atlas CH-4 mass spectrometer no peak at *m/e* 570 could be detected.

2,6,2′,6′,2′′,6′′-Hexamethoxytriphenylmethyl (II) (HMTPM). A solution of the corresponding carbonium ion was prepared by dissolving 3.35 g of 2,6,2′,6′,2′′,6′′-hexamethoxytriphenylcarbinol (0.0076 mole) in 80 ml of 10% sulfuric acid. The resulting purple solution was poured into a separatory funnel and 50 ml of ether added. A saturated solution of chromium sulfate (slightly acidic) was passed through a Jones Reductor and the chromous ion solution allowed to drop into the separatory funnel. During the addition of chromous ion, the ether layer became deep red in color. The addition was carried out until the purple color of the aqueous layer had disappeared. The ether layer was washed with sodium bicarbonate solution and water and dried over magnesium sulfate. The aqueous layer was extracted with ether and the ether layer washed and combined with the previous ether extract. Removal of ether under reduced pressure yielded 3.0 g (94%) of crude II, mp 132–136° dec (resolidified and remelted 190–200°). Purification of the radical was accomplished by sublimation under a high vacuum using an oil bath preheated to 140°. Recovery was usually in the range of 10–30% of material, mp 132–136° (resolidified and remelted 190–200°). *Anal.* Calcd for $C_{25}H_{27}O_6$: C, 70.90; H, 6.44. Found: C, 70.72; H, 6.42.

In recrystallization of this material some of the radical was always destroyed, yielding an insoluble gum, as the solid was dissolved in the recrystallization solvent. Quantitative ultraviolet spectra were obtained on samples directly extracted from the reaction medium with extinction coefficients calculated assuming quantitative conversion of carbonium ion to radical and quantitative extraction. The quoted values should, therefore, be viewed as lower limits. The spectra so obtained contained no peaks not seen in spectra of sublimed material. In ether solution a Beer's law plot was linear from 3.6×10^{-5} to 9.6×10^{-5} *M* [λ_{max} 364 mμ (log ε 4.30); in benzene λ_{max} 370 mμ (log ε 4.44)]. The mass spectrum showed the expected molecular ion peak at *m/e* 423.

Resorcinol Dimethyl-d_6 Ether. Resorcinol (8.8 g, 0.08 mole) in 50 ml of dry tetrahydrofuran (distilled from $LiAlH_4$) was added to sodium hydride (8.5 g, 0.18 mole of 50.6% NaH) in 100 ml of tetrahydrofuran over a period of 5 hr. The reaction mixture was added slowly (10 hr) with stirring to dimethyl-d_6 sulfate (>99% D) (10.0 g, 0.08 mole) under a nitrogen atmosphere. The reaction mixture was boiled for 24 hr. The reaction mixture was extracted with 20% NaOH until the aqueous extract was colorless. The resulting oil was taken up in ether and dried over magnesium sulfate. Removal of the ether and distillation of the remaining oil yielded 4.41 g (80%) of product, bp 99–101° (18 mm). The infrared spectrum (10% CCl_4) showed C–D stretching in the range 2280–2060 cm^{-1} and very weak C–H stretching bands in the range 3110–2860 cm^{-1}. *Anal.* Calcd for $C_8H_4D_6O_2$: D, 60.00 atom %. Found: D, 58.90 atom %.

2,6,2′,6′,2′′,6′′-Hexamethoxy-d_{18}-triphenylcarbinol. The method described previously[4] for the isotopically normal carbinol was used to give material, mp 164.5–165°, showing infrared absorption at 2280–2040 cm^{-1} and an nmr spectrum identical with that of the protonic material but lacking the methoxyl absorption at τ 6.58. *Anal.* Calcd for $C_{24}H_{10}D_{18}O_7$: C, 65.46; H, 6.18; D, 64.29 atom %. Found: C, 65.44; H, 6.34; D, 64.8 atom %.

2,6,2′,6′,2′′,6′′-Hexamethoxy-d_{18}-triphenylmethyl. A solution of the carbonium ion from the above carbinol (0.216 g in 40 ml of 10% sulfuric acid) was treated with chromous ion as described in the synthesis of II. The yield of crude material was 70%. The crude radical was sublimed under high vacuum at an oil bath temperature of 140° to give 30 mg of product used in the esr studies.

Preparation of Bis(2,6-dimethoxyphenyl) Ketone-^{13}C. A suspension of 2,6-dimethoxybromobenzene[7] (5.64 g, 0.026 mole) in 35 ml of sodium-dried ether and an excess of lithium wire (0.6 g, 0.09 g-atom) were refluxed for 40 hr. The ^{13}C-enriched carbon dioxide was generated at atmospheric pressure from 54% ^{13}C-enriched barium carbonate (0.844 g, 0.00428 mole) by the addition of 50% aqueous perchloric acid using prepurified nitrogen as the sweep gas. It was collected in U-tube traps cooled with liquid nitrogen. The perchloric acid (40 ml) was added at the rate of one drop per 20 sec until the carbonate was consumed. The remainder was added rapidly and the system purged with nitrogen for an additional 10 min. The system was evacuated, and the contents of the two traps, 0.0042 mole (98%), were distilled into the reaction vessel. The vessel was brought to near atmospheric pressure with N_2, and the solution was refluxed for 1 day. It was then poured onto ice through a funnel containing a glass bead to remove excess lithium. Filtration and drying yielded 1.06 g of crude ketone, mp 200–205°. Recrystallization from benzene gave 0.85 g (67%) of bis(2,6-dimethoxyphenyl) ketone-^{13}C (54% enrichment), mp 205.5–207° (lit.[8] mp 205.4–206.2°).

Preparation of 2,6,2′,6′,2′′,6′′-Hexamethoxytriphenylcarbinol-^{13}C. The addition of 2,6-dimethoxyphenyllithium to bis(2,6-dimethoxyphenyl) ketone-^{13}C (0.79 g, 0.0026 mole) was carried out by the published[4] procedure to give 0.71 g (62%) of the carbinol, mp 164–165° (lit.[4] mp 165–166).

Preparation of Triphenylcarbinol-^{13}C. The procedure used was similar to that just described. In this case phenyllithium solution in ether was added to the carbon dioxide (0.0042 mole, 56% ^{13}C) in the reaction vessel *via* hypodermic syringe and serum stopple. Recrystallization of the triphenylcarbinol-^{13}C from CCl_4 gave 0.36 g (33%), mp 160–161°.

Preparation of Triphenylmethyl-^{13}C. Triphenylchloromethane-^{13}C was prepared from the carbinol by the method of Bachmann.[9] The chloro derivative (0.024 g, 0.000086 mole) in 2 ml of dry benzene

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[5] We wish to acknowledge the assistance of Mr. O. W. Norton, Mr. D. Johnson, Mr. J. Nemeth, and associates for infrared and nmr spectra and elemental analyses. Dr. T. H. Kinstle kindly provided the mass spectra.

[6] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p 149.

[7] H. Lettre and A. Jahn, *Chem. Ber.*, **85**, 346 (1952).

[8] G. Wittig and U. Pockels, *ibid.*, **72B**, 89 (1939).

[9] W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 841.

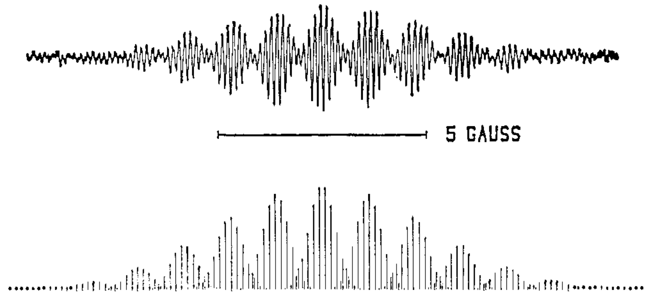


Figure 1. Experimental and calculated esr spectra of 2,6,2′,6′,-2′′,6′′-hexamethoxytriphenylmethyl radical (II).

was placed in the reaction vessel and the solution degassed. Zinc dust (50 mg), contained in a side arm, was then added to the benzene solution, and the reaction mixture was shaken for 15 min. The yellow solution of triphenylmethyl-^{13}C (56% enrichment) in benzene was filtered through sintered glass into an esr sample tube, which was a part of the reaction vessel, and the tube sealed under vacuum.

Electron Spin Resonance Studies. A Varian V-4500 spectrometer with 100-kc modulation was used in most of these experiments. The magnetic field was provided by a Varian V-4007 6-in. electromagnet with shimmed pole caps. Our sweep unit, which has been described elsewhere,[10] produced a sweep of the magnetic field by supplying an input signal to the V-2200 magnet power supply. A transistorized nmr detector, which incorporated a modified version of the circuit described by Singer and Johnson,[11] was used to calibrate each of the spectra. The spectra of the ^{13}C-enriched samples were obtained using a Varian V-4502 spectrometer using a dual-cavity setup with a dual-channel recorder. Spectra were calibrated directly by comparison with a standard sample of Fremy's salt.[12]

Each sample was sealed in a 4-mm Pyrex tube after going through at least four freeze-pump cycles to remove oxygen. Sesquixanthydryl dimer III was found to be only very slightly soluble in most solvents. Even a 3 × 10^{-5} M solution of the dimer in anhydrous diethyl ether probably contained some of the solid compound in suspension. This solution exhibited a weak, broad, and asymmetric esr signal. No signal was detected from a much more concentrated solution which had been prepared by heating the solid compound in diethylene glycol dimethyl ether. In order to increase the degree of dissociation, this solution was heated to 150° in the esr cavity. Under these conditions a broad, weak signal was detected which may have resulted from some impurity. No signals were detected in a sample of crystalline III in a standard, 4-mm tube.

Radical II also was dissolved in anhydrous diethyl ether to make a 3 × 10^{-5} M solution. The esr signal of this solution was found to consist of nine overlapping lines. We measured the g value to be 2.0028 by using an internal capillary of DPPH as a reference. Upon reducing the microwave power and the modulation amplitude, each of these lines split into an array of hyperfine components. Concentration was also found to be an important factor in determining the line widths. The radicals were not stable in the sealed tubes, and a marked decrease in concentration was noted after a few days. In order to obtain the optimum concentration, esr spectra were recorded after allowing the solutions to stand for various intervals of time. Figure 1 shows the best resolution that was obtained by this technique. Line widths in this spectrum are about 70 mgauss which is close to the theoretical limit for a system employing 100-kc modulation.[13] The compound with deuterated methoxy groups was treated in the same fashion and its spectrum is shown in Figure 2.

Results

The chromous ion reductions of the corresponding carbonium ions[4] lead directly to the triarylmethyl radical II and, presumably through the sesquixanthydryl radical I, to dimer III. The highly *ortho*-substituted II (HMTPM) is sufficiently unreactive toward oxygen that good yields of the radical can be obtained even without excluding oxygen during the preparation.

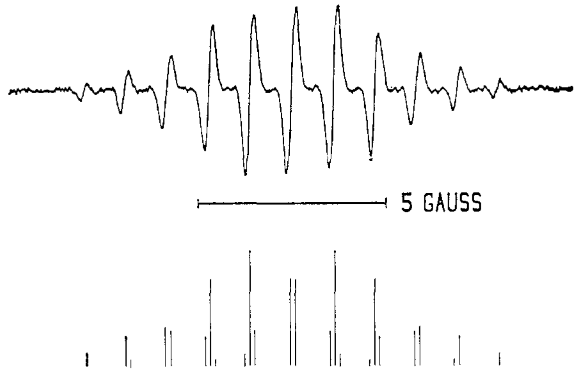
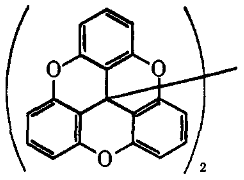


Figure 2. Experimental and calculated esr spectra of 2,6,2′,6′,-2′′,6′′-hexamethoxy-d_{18}-triphenylmethyl radical.

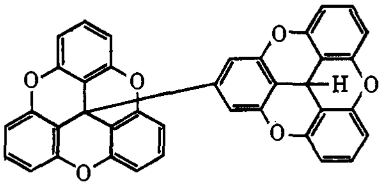
Radical II does react slowly with oxygen, over a period of hours in solution, though the position of attack is not known. Treatment with trifluoroacetic acid of the red-brown product formed by the reaction with oxygen regenerates the purple hexamethoxytriphenylcarbonium ion.[4] Protonation of a peroxide linkage at either the central carbon or one of the *ortho* or *para* ring positions might be expected to lead to this carbonium ion. Solutions of II in ether or benzene are red-orange in color [λ_{max} 370 mμ (log ϵ 4.44) in benzene]. Exposure to air results in the decrease and, eventual disappearance of the 370-mμ absorption. Oxygen-free solutions in ether at room temperature show a slowly decreasing esr signal up to 3 weeks after preparation.

The poor solubility of III in almost all solvents made its characterization difficult. A strong mass peak at m/e 285, characteristic of the very stable[4] sesquixanthydryl cation, is the highest mass peak seen. No molecular ion peak is observable even at low ionizing voltages. The dimeric nature of III is inferred from its diamagnetism and its elemental composition. It is difficult to conceive of reasonable structures for III which are other than dimeric (*i.e.*, polymeric, tetrameric, etc.).

The sesquixanthydryl cation can be regenerated from III by suspending III in trifluoroacetic acid and exposing it to a stream of oxygen. These results are compatible with a structure such as IV for the dimer, but do not rule out possible structures, such as V, involving dimerization at the *para* positions of I.



IV



V

The reaction of I, from the dissociation of IV, with oxygen in acid solution provides a possible route to the observed sesquixanthydryl cation. Solutions of III in methyl benzoate reversibly acquire a light green color on heating to the boiling point, an observation which one is tempted to attribute to the radical I. No well-

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(10) D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *J. Chem. Phys.*, 32, 196 (1960).

(11) J. R. Singer and S. D. Johnson, *Rev. Sci. Instr.*, 30, 92 (1959).

(12) For which a value of a_N = 13.0 ± 0.1 gauss is reported; personal communication from J. S. Hyde to J. Q. Adams; and J. R. Thomas, *J. Chem. Phys.*, 39, 1904 (1963).

(13) J. S. Hyde and H. W. Brown, *ibid.*, 37, 368 (1962).

defined esr signals could be seen in solutions of III, however, either at room temperature or at 150° in diglyme.

We may explain the gross features of the spectrum of II (Figure 1) by assigning a hyperfine splitting constant to the *ortho* protons that is twice as large as the one that is assigned to the *meta* protons. The additional fine structure can then be attributed to the methyl protons which must have a splitting constant either equal to the smallest spacing in the spectrum or equal to some multiple of it. This analysis can be refined by noticing that the central group of hyperfine components has no center line while the next two groups out from the center on either side do have such a line. A pattern of this type can arise if the splitting constant for the *para* protons is slightly greater than or slightly less than two times the *meta* splitting constant. In order to decide which is the case, ten spectra were calibrated and their spacings averaged. Several theoretical spectra were then constructed with different values for the splitting constant of the methyl protons. The best theoretical spectrum, which is shown directly below the experimental spectrum in Figure 1, was obtained with the splitting constants shown below.

$$a_H\ (para) = 2.26 \pm 0.02 \text{ gauss}$$

$$a_H\ (meta) = 1.06 \pm 0.01 \text{ gauss}$$

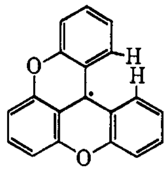
$$a_H\ (OCH_3) = 0.14 \pm 0.01 \text{ gauss}$$

In order to confirm this assignment, we obtained the esr spectrum for radicals which were identical with those obtained from II except that the methyl groups were entirely deuterated. This deuterium substitution should reduce the splitting constant for the methyl group by a factor of 0.153[14] and, therefore, produce a splitting too small to be resolved in this experiment. These unresolved components should produce an appreciable line width for the remaining lines in the spectrum. This effect is shown in the experimental spectrum in Figure 2. Within experimental error all of the spacings are the same and are equal to 1.11 ± 0.04 gauss. The theoretical spectrum in the lower half of Figure 2 was constructed using the *meta* and *para* splitting constants given above. Even though the smaller spacings are not resolved, their presence is clearly indicated by the asymmetric first derivative traces of some of the lines in the experimental spectrum.

Spectra of samples of II and of the unsubstituted triphenylmethyl radical VI, enriched (54% for II, 56% for VI) with ^{13}C at the central carbon, were obtained at high modulation amplitude (13.0 gauss) so that the proton hyperfine structure was removed. The resulting spectra consisted of three overlapping lines. It proved possible to decompose these spectra into their component lines by assuming identical shapes for the central line and the two ^{13}C satellites, with relative intensities calculated from the known level of isotopic labeling. Spectra reconstructed by adding the three lines so obtained were in excellent agreement with the experimental spectra. These gave values for a_C of 26.2 ± 0.5 gauss for II and 23.0 ± 0.8 gauss for VI.

Discussion

The report by Neunhoffer and Haase[15] of the doubly *ortho*-bridged radical VII is interesting, since the radical



VII

is reported to be very oxygen sensitive and is extensively dissociated even in the crystalline state. The two remaining *ortho* protons in the molecule interact to prevent a completely planar structure for the radical, and this unfavorable steric interaction is intensified as the hybridization about the central carbon approaches sp^3 in the formation of the dimer. This contrasts markedly with the sesquixanthydryl group which appears, from an inspection of molecular models, to possess little angular strain in the planar radical or in the presumably tetrahedral dimer, IV. It is clear that the increased resonance stabilization of I, attributable to its planar geometry, is more than offset by the large decrease in the repulsive steric interactions in the dimer, relative to those in most hexaarylethanes.[16] The early noted[3b] greatly increased association of 9-phenylfluorenyl radicals, as compared with triphenylmethyl radicals, may reflect a similar decreased steric interaction. In constrast, the introduction of oxygen bridges between phenyl rings to form the xanthydryl ring system has been found[3c,15] in several systems to result in increased dissociation of the ethane. The propeller model[17] for the conformations of trityl derivatives has been generally[18] used in attempts to treat theoretically the observed[19–21] esr spectrum of triphenylmethyl. The variation of spin density with angle of twist has been calculated[18] for the trityl radical by both valence bond[21] and approximate SCF theory.[22] Agreement with experiment is not completely satisfactory with either treatment. Most calculations[18,21,23] suggest an angle of twist for the phenyl rings of about 30°, in keeping with that found[24] by X-ray crystallographic structure determination of 4,4′,4′′-trinitrotriphenylmethyl.

With some trepidation we have used the simple Hückel MO method to estimate the increase in angle of twist for HMTPM (II) over that for triphenylmethyl (TPM).[25,26] In this application to a nonplanar system

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[14] B. Venkataraman and G. K. Fraenkel, *J. Chem. Phys.*, **24**, 737 (1956).

[15] O. Neunhoffer and H. Haase, *Chem. Ber.*, **91**, 1801 (1958).

[16] Independent evidence for this increase in stability of the dimer III is seen in measurements of the electrical potential for the sesquixanthydryl cation–radical couple: R. A. Diffenbach, K. Sano, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 4747 (1966).

[17] G. N. Lewis and M. Calvin, *Chem. Rev.*, 25, 273 (1929).

[18] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961), and references contained therein.

[19] D. B. Chesnut and G. J. Sloan, *ibid.*, 33, 637 (1960); see also J. S. Hyde, *ibid.*, 43, 1806 (1965), for slightly different hfs constants obtained by the ENDOR method.

[20] P. B. Ayscough, A. P. McCann, and R. Wilson, *Proc. Chem. Soc.*, 16 (1961).

[21] F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 2057 (1958).

[22] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[23] F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

[24] P. Anderson and B. Klewe, *Acta Chem. Scand.*, **16**, 1817 (1962).

[25] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 161.

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uncertainty about the validity of the π-electron approximation is added to the well-known defects of the Hückel calculation; but we have nevertheless assumed the approximate proportionality of the calculated spin densities to the measured hyperfine splitting constants, at least for positions of high spin density. Thus the measured splitting constant for the *para* protons can be related to the calculated *para* spin density by McConnell's equation,[27] $a_{\mathrm{H}} = Q\rho$. The twist angle is introduced by using $\beta \cos \theta$ for the resonance integral between the central carbon atom and the adjacent carbon atom in each ring,[28] where β is the resonance integral between neighboring carbon atoms in benzene and θ is the angle between the plane of one of the phenyl rings and the plane of the central carbon and its bonds. Spin densities are then obtained as functions of θ. If we assume that $\theta = 30°$ for TPM and use 2.77 and 2.26 gauss for the *para*-proton splitting constants for TPM and HMTPM, respectively, we find that an additional 17 degrees of twist is present in HMTPM.

This increase in the angle of twist predicts, on the same model, an increase in a_{C} at the central position by a factor of 1.31. We observe an increase by a factor of 1.14. It should be noted that our value for a_{C} for TPM (23.0 ± 0.8 gauss) is somewhat lower than the more recent literature values,[20,21,29] which suggest 25–26 gauss. The factor of 1.14 quoted for the ratio of a_{C} values for HMTPM and TPM was obtained from two measurements made in exactly the same way, using the same calibration methods, so the ratio should be more reliable than the individual values. In any event, it is clear that a_{C} is larger for HMTPM than it is for TPM.

While it is true that the introduction of six *o*-methoxyl substituents will modify the molecular electronic structure, even in the absence of the steric effect upon which we have focussed our attention, literature analogies[30-32] suggest that the reduction in a_{para} from 2.77 to 2.26 is substantially larger than would be expected for such an electronic substituent effect. A series of several *para*- and *meta*-substituted triphenylmethyls with a variety of substituents (F, Cl, Br, I, CH_3, OCH_3, NO_2) show[33-35] a_{para} to fall in the range 2.75–2.85; a_{meta}, 1.05–1.15; and a_{ortho}, 2.50–2.89 gauss. It seems probable, therefore, that the low value of a_{para} in II reflects mainly a decrease in spin delocalization attributable to the increase in pitch of the propeller conformation of HMTPM induced by the six *ortho* substituents. There is still the troublesome fact that the increase of a_{C} in II compared to TPM is appreciably less than that predicted on the basis of the a_{H} (*para*) values. The discrepancy, however, may result from the sensitivity of a_{C} to substituent effects inasmuch as the introduction of three *p*-methoxyl substituents in TPM decreases a_{C} to 22.9 gauss,[35] but an increase to 26.2 gauss is seen when six *o*-methoxyls are introduced.

Some additional information about the steric interactions in II is contained in the a_{H} found for the methoxy-group protons. When a methoxy group is substituted for an hydrogen atom in an aromatic molecule the ratio of the splitting constants of the methoxy protons to that of the replaced proton is about $^1/_{10}$[30-34] or even greater.[36,37] In the HMTPM radical this ratio is substantially less, only about $^1/_{20}$. The conformational equilibria involving rotation about the bonds linking the aromatic ring and the methoxyl oxygen are affected by steric factors in the highly hindered radical II, and the hyperfine coupling to methoxyl protons in it is averaged over ranges of angles different from those prevailing in a less hindered molecule. Thus, the small coupling to methoxyl protons in II represents a combination of conformational differences due to steric effects and the dependence of a_{H} (OCH_3) upon the rotational angle about the oxygen-aromatic ring bond.

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