propylphenyl)pentane. 2-Lithio-2-(4-isopropylphenyl)-4,4-dimethylpentane, prepared from *p*-isopropyl-α-methylstyrene (0.05 mol) as described above, was allowed to react with a tenfold excess of water.

The reaction mixture was extracted with diethyl ether and the extract washed subsequently with 1 *N* HCl until the aqueous layer was acidic in order to remove TMEDA and then washed with distilled water several times. The ether layer was separated, dried over $MgSO_4$, and concentrated on a rotary evaporator under vacuum. The 1:1 adduct, 2,2-dimethyl-4-(*p*-isopropyl)phenylpentane, was obtained by vacuum distillation, yield 7.37 g (67.7%), based on *p*-isopropyl-α-methylstyrene, bp 103–104° (4.3 mm). The mass spectrum showed M^+ 218.

2,2-Dimethyl-4-phenylpentane. This compound was obtained in 68% yield, according to the above procedures starting from 0.05 mol of α-methylstyrene followed by hydrolysis, bp 77–77.5°(6.3 mm), M^+ 176.

2,2-Dimethyl-4-(*p*-*tert*-butylphenyl)pentane. From 8.7 g of *p*-*tert*-butyl-α-methylstyrene, according to the above procedure, was obtained 9.4 g, 81% yield, of the title compound, bp 103–105° (2.2 mm), M^+ 232.

2,2-Dimethyl-4-phenylpentane-*4-d*. The procedure was identical with that described above except the benzyllithium solution was hydrolyzed with D_2O. Vacuum distillation gave 5.2 g, 58.6% yield, of product, bp 78–78.5° (6.7 mm), M^+ 177.

2,2-Dimethyl-4-(*p*-isopropyl)phenylpentane-*4-d*. The procedure was identical with that described above except the benzyllithium solution was hydrolyzed with D_2O. Vacuum distillation gave 8.0 g, 73.2% yield, bp 106–107° (4.9 mm), M^+ 219.

2,2-Dimethyl-4-(3,5-di-*tert*-butyl)phenylpentane-4-*d*. The α-methyl-α-neopentyl-(3,5-di-*tert*-butyl)benzyllithium solution was prepared from the reaction of 6.9 g of 3,5-di-*tert*-butyl-α-methylstyrene with *tert*-butyllithium. The red solution containing some orange precipitate was hydrolyzed with D_2O and worked up with diethyl ether as usual. Distillation under reduced pressure gave 6.6 g (76.2%) of product, bp 113.5–115° (1.5 mm), M^+ 289.

2,2-Dimethyl-4-(*p*-isopropyl)phenyl-4-trimethylsilanylpentane. The appropriate benzyllithium solution prepared as described above was allowed to react with 1 equiv of trimethylchlorosilane. The work-up procedure was the same as that described above. Vacuum distillation gave 10.6 g (73.1%), bp 90–91° (0.1 mm). The mass spectrum showed M^+ 290.

Acknowledgment. This research was supported in part by the National Science Foundation Grant No. 16402. Also nmr apparatus used in this work was purchased in part with a grant from the National Science Foundation.

An Electron Spin Resonance Study of the Phosphorescent States of Some 4- and 4,4′-Substituted Biphenyls

Harriet V. Taylor,[1] A. L. Allred,* and Brian M. Hoffman[2]

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201.
Received August 21, 1972

Abstract: Substituent effects on the unpaired spin distribution of the phosphorescent state for a series of 4- and 4,4′-substituted biphenyls were studied by epr and phosphorescence spectroscopy. No net differences in either epr or phosphorescence results are seen among the various alkyl substituents. Examination of zero-field splitting parameters suggests partial transfer of π-electron spin density from aromatic rings to silyl and germyl groups. Line-width variation among CH_3, CD_3, and CF_3 derivatives is explained by hyperfine interaction with substituent nuclei. The triplet state epr and phosphorescence results are supported by previously reported polarographic and uv data and by MO theory.

The influence of substituents on an aromatic π-electron system has been the subject of study for many years among organic chemists. Several orderings of electron donating and withdrawing effects have been proposed for many substituents based on studies of acidity or reactivity.[3–8] It is also of interest to determine the effect of these groups when the molecules are not undergoing reaction, since in many cases the influences on reactivity can be attributed to steric interactions or solvation effects.

Substituent effects are here reported for the first excited triplet state of several 4- and 4,4′-substituted biphenyls. Similar studies have been reported for methyl-substituted naphthalenes.[9] Triplet state energies are obtained from phosphorescence spectra. Electron paramagnetic resonance is used to obtain a measure of the changes in the triplet state spin density distribution caused by substituents on biphenyl and also to obtain triplet state lifetimes. Changes in the triplet spin density are reflected by changes in the zero-field splitting (ZFS) parameters *D* and *E* which characterize the dipolar spin Hamiltonian. With the addition of an isotropic Zeeman interaction, the Hamiltonian can be expressed as[10]

$$\hat{H}_D = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$$

The parameter *D* is a measure of the distance between unpaired triplet spins averaged over the triplet wave function ($D \propto \langle r_{12}^{-3} \rangle$), and thus *D* gives a measure of

---

[1] National Institutes of Health Predoctoral Research Fellow.

[2] Alfred P. Sloan Fellow.

[3] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[4] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

[5] W. M. Schubert, J. M. Craven, R. G. Minton, and R. B. Murphy, *Tetrahedron*, 5, 194 (1959).

[6] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.

[7] R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 74, 3120 (1952).

[8] C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[9] B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, **46**, 3976 (1967).

[10] J. E. Wertz and J. R. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications," McGraw-Hill, New York, N. Y., 1972.

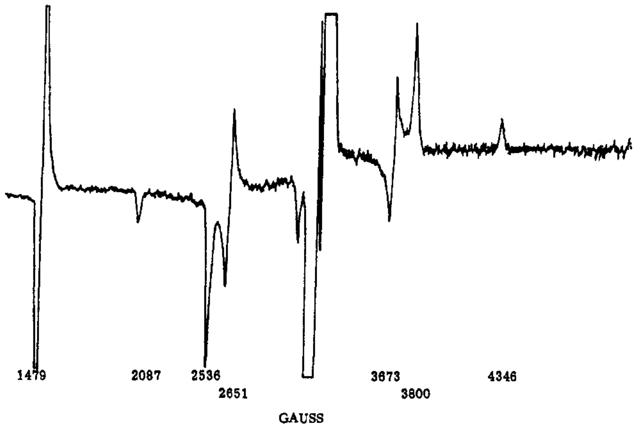

Figure 1. Epr spectrum of the first excited triplet state of 4,4′-dimethylbiphenyl showing the $\Delta M = \pm 2$ (1479 G) and the six $\Delta M = \pm 1$ transitions.

the spatial distribution of triplet spin density to complement the energy information from phosphorescence studies. E is a measure of the in-plane anisotropy of the spin distribution, being zero for an aromatic molecule with threefold or greater symmetry.

Experimental Section

Samples of the substituted biphenyls with the exception of those mentioned below were prepared previously in this laboratory[11,12] or were purchased commercially and used without further purification after verification of melting points: 4,4′-dimethylbiphenyl (Aldrich Chemical Co., mp 123°, lit.[13] 125°); 4,4′-dihydroxybiphenyl (Eastman Organic Chemicals, mp 272–274°, lit.[13] 274–275°); and 4-hydroxybiphenyl (Eastman Organic Chemicals, mp 164–165°, lit.[13] 165–167°).

4,4′-Diethylbiphenyl was synthesized from 4,4′-dilithiobiphenyl and ethyl iodide,[11] mp 79–81° (lit.[11] 78–80°).

4,4′-Dimethoxybiphenyl was synthesized by the Williamson ether synthesis[14] from *p,p*′-biphenol, mp 176–178° (lit.[13] 173°).

4,4′-Bis(trifluoromethyl)biphenyl resulted from the coupling reaction of *p*-iodobenzotrifluoride with copper bronze,[15] mp 92–94° (lit.[16] 91–94°).

Phosphorescence Spectroscropy. Samples of the substituted biphenyls at 10^{-2} *M* in EPA (Matheson Coleman and Bell; a 5:5:2 v/v solution of ethyl ether, isopentane, and ethanol) were placed in 4 or 5 mm o.d. quartz tubes; degassing was found to be unnecessary. Spectra were obtained with a phosphorescence accessory on a Hitachi (Perkin-Elmer) Model MPF-2A fluorescence spectrophotometer containing the quartz sample tube immersed in liquid nitrogen.

Electron Spin Resonance Spectroscopy. Solutions of the substituted biphenyls (~0.1 *M*) in EPA were placed in 4 or 5 mm o.d. quartz tubes without degassing. 4,4′-Di-*tert*-butylbiphenyl was also examined in 2-methyltetrahydrofuran, ethanol, and cyclohexane.

Spectra were taken on a Varian Associates Model E-4 spectrometer with the microwave field perpendicular to the static magnetic field. Field positions were measured from the E-4 calibrated chart paper, whose linearity over a 2000-G scan was checked with Mn^{2+} in MgO. The operating frequency was calculated from the field of the solvent peak ($g = 2.00$) for each sample and was approximately 9.07 GHz. A Hanovia 200-W Xe–Hg arc, equipped with water filter, was used as the irradiation source. All spectra were taken with the sample in boiling liquid nitrogen except for one variable-temperature study (of 4,4′-di-*tert*-butylbiphenyl in diethyl ether) which employed a conventional variable-temperature apparatus using cold nitrogen gas.

Electron spin resonance spectra for all substituted biphenyls studied, except those noted below, showed the characteristic six $\Delta M = \pm 1$ transitions centered about $g = 2.00$ plus the low-field $\Delta M = 2$ peak.[17] See Figure 1 for a representative spectrum.

From the spectrometer frequency and the canonical $\Delta M = \pm 1$ line positions, D, E, and g values were calculated by an iterative procedure using published equations.[10,17,18] Calculation was terminated when D and E remained constant to within ±0.0001 cm^{-1}. Molecular axis assignments followed those of Baiwir[19] and Mispelter:[20] the longer in-plane axis is the x direction, the shorter axis y, and z is perpendicular to the molecular plane.

Triplet State Lifetimes by Epr. Samples similar to those above were placed in 4 or 5 mm o.d. quartz tubes with Teflon valves and degassed three times by the freeze–pump–thaw method to remove molecular oxygen. Phosphorescent lifetimes, $\tau_p{}^0$, were obtained by recording the time decay of the $\Delta M = 2$ epr signal after the irradiation was interrupted. The logarithm of the signal intensity was plotted as a function of time, and a least-squares fit to the equation $\ln (I - I_\infty) = (-t/\tau_p{}^0) + C$ was performed for those samples which gave straight lines.

Results

Phosphorescence spectra for the substituted biphenyls consist of two well-defined intense bands and two long wavelength shoulders. The frequencies of the shortest wavelength band, or the 0,0 transition, are shown in Table I.

Table I. Phosphorescence Energies and Lifetimes and Zero-Field Splitting Parameters for Some 4- and 4,4′-Substituted Biphenyls in EPA at 77°K

	$^3\lambda(0,0) \times 10^{-4}$ cm^{-1}	$\tau_p{}^0$, sec	D, cm^{-1}	$-E$, cm^{-1}
1. Biphenyl	2.29 ± 0.01	4.3 ± 0.2	0.1091 ± 0.0002	0.0035 ± 0.0002
2. Dimethyl	2.25	4.4	0.1054	0.0040
3. Bis(trideuteriomethyl)	*a*	4.5	0.1060	0.0037
4. Bis(trifluoromethyl)	2.40	4.1	0.1082	0.0046
5. Diethyl	2.25		0.1058	0.0040
6. Diisopropyl	2.25		0.1060	0.0040
7. Di-*sec*-butyl	2.25		0.1059	0.0038
8. Di-*tert*-butyl	2.25	4.7	0.1059[c] 0.1059[d]	0.0040[c] 0.0080[d]
9. Bis(trimethylsilyl)	2.22	2.9	0.1024	0.0063
10. Bis(trimethylgermyl)	2.23	*b*	0.1055	0.0040
11. Trimethylsilyl	2.24	3.5	0.1051	0.0051
12. Trimethylgermyl	2.25	*b*	0.1073	0.0039
13. Difluoro	2.30	3.0	0.1127	0.0000
14. Dimethoxy	2.21	1.3	0.1027	0.0026
15. Dihydroxy	2.20	*b*	0.1021	0.0031
16. Hydroxy	2.24	3.0	0.1041	0.0041

[a] Similar to other dialkylbiphenyls but poorly resolved. [b] Plot of $\ln (I - I_\infty)$ *vs.* time was nonlinear. [c] Measured from the peaks due to the more populated site. [d] Measured from the peaks due to the less populated site.

The difference in energy between the first singlet excited state and the singlet ground state ($S_0 \rightarrow S_1$) as measured by uv absorption spectroscopy is essentially constant for all the alkyl-substituted molecules, as previously reported,[11] and is smaller than the $S_0 \rightarrow S_1$ difference in parent biphenyl. Other substituents for which there exists a mechanism for electron delocaliza-

---

(11) A. L. Allred, L. G. Newman, and D. E. Smith, to be submitted for publication.

(12) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, **87**, 2554 (1965).

(13) "The Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Co., Cleveland, Ohio, 1969, p C-205.

(14) R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966, pp 562–564.

(15) A. I. Vogel, "A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis," 3rd ed, Wiley, New York, N. Y., 1956.

(16) M. R. Pettit and J. C. Tatlow, *J. Chem. Soc.*, 1071 (1954).

(17) P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **41**, 379 (1964).

(18) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(19) M. Baiwir, *Chem. Phys. Lett.*, **9**, 482 (1971).

(20) J. Mispelter, *Chem. Phys. Lett.*, **10**, 539 (1971).

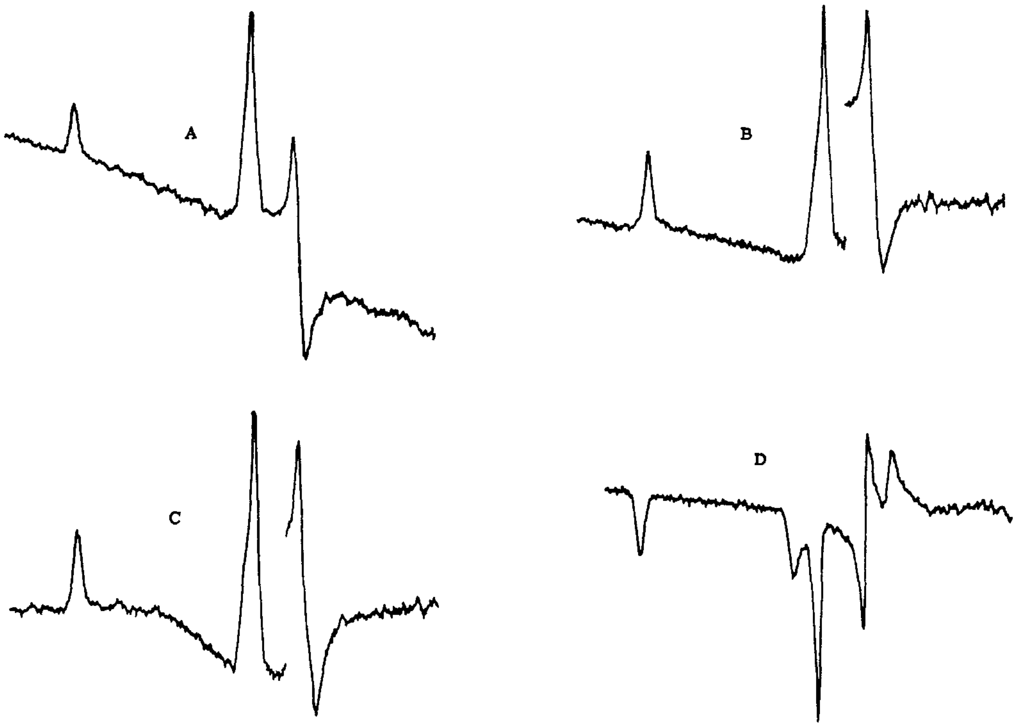

Figure 2. Epr spectra of the first excited triplet states of (A) 4,4′-diethylbiphenyl, (B) 4,4′-diisopropylbiphenyl, (C) 4,4′-di-*sec*-butylbiphenyl, and (D) 4,4′-di-*tert*-butylbiphenyl. Only the low-field half of the $\Delta M = \pm 1$ peaks is shown.

tion also have lower transition energies than the parent. These include the silicon, germanium, and oxygen-containing derivatives.

Table I shows that upon substitution the energy difference between the first excited triplet state and the singlet ground state, $E(S_0 \rightarrow T_1)$, follows the same trend as $E(S_0 \rightarrow S_1)$, although the differences between compounds are smaller for the $S_0 \rightarrow T_1$ than for the $S_0 \rightarrow S_1$ transitions both for the alkyl and organometallic derivatives. For the organometallic compounds, one substituent has approximately half the effect of two, but such is not the case for the hydroxyl compounds (Table I).

Phosphorescence Lifetimes. For most of the substituted biphenyls, decay of the triplet state signal was governed by a single exponential process, and the derived lifetimes are listed in Table I. It is seen that substitution on the aromatic system decreases the lifetime and that this decrease is dependent upon the atomic number of the bonded atom for the $M(CH_3)_3$ derivatives. This result suggests that there is a contribution to the decay probability from unpaired spin density on the substituent, with the decrease in the lifetimes of the trimethylmetal derivatives with increasing atomic number reflecting a corresponding increase in spin–orbit coupling.

In several cases, notably 4,4′-dihydroxy-, 4,4′-bis(trimethylgermyl)-, and 4-trimethylgermylbiphenyl, a plot of ln $(I - I_\infty)$ *vs.* time was not linear, but seemed to be biphasic. The decay of these molecules also appeared to be appreciably faster than for those reported above. Proposed sources of[21] biphasic decay of excited triplets include chemical reactivity in the excited state and microscopic heterogeneity in solvation, with different lifetimes associated with different sites in the mixed polarity solvent EPA.

Electron Spin Resonance Spectra. Values of D and E for all molecules studied, calculated by the method described above, are presented in Table I. The calculated g values were equal in all cases to 2.00 and isotropic within the accuracy of the experiment. The ZFS parameters for biphenyl in EPA (Table I) agree closely with literature values (0.1092, -0.0036 cm^{-1} in diethyl ether;[22] 0.1094, -0.0036 cm^{-1} in ethanol;[23] 0.1096, -0.0035 cm^{-1} in ethanol[24]). The precision of the parameters reported in this work is ± 0.0002 cm^{-1}.

As can be seen in Table I, D for the 4,4′-dialkylbiphenyls is lower in all cases than for the parent hydrocarbon but is constant within experimental error among these substituted molecules. D for the digermyl derivative is similar to that for the di-*tert*-butyl compound, but D for the disilyl case is considerably lower. Differences in D between parent and substituted molecules doubled in going from mono- to disubstituted silyl and germyl derivatives.

The E parameters for the *tert*-butyl and germyl derivatives are just slightly larger than for the parent biphenyl, indicating that the in-plane symmetry of the two-electron spin distribution is not appreciably disturbed when these two substituents are attached to the biphenyl moiety. The much larger E for the silicon analog again indicates a more substantial rearrangement of triplet spin by $SiMe_3$.

Comparison of 4,4′-dimethoxybiphenyl and 4,4′-dihydroxybiphenyl indicates that the OH substituent

---

(21) P. R. Callis and R. W. Wilson, *Chem. Phys. Lett.*, **13**, 417 (1972); M. Koyanagi, R. Zwarich, and L. Goodman, *J. Chem. Phys.*, **56**, 3044 (1972).

(22) S. Siegal and H. S. Judeikis, *J. Phys. Chem.*, **70**, 2201 (1966).

(23) Y. Gondo and A. H. Maki, *J. Phys. Chem.*, **72**, 3215 (1968).

(24) J. Mispelter, J.-Ph. Grivet, and J.-M. Lhoste, *Mol. Phys.*, **21**, 1015 (1971).

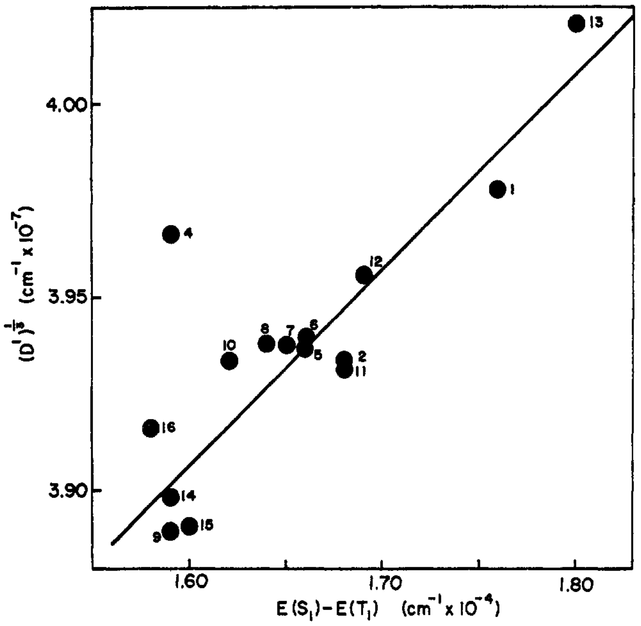

Figure 3. $(D')^{1/3}$ *vs.* $[E(S_1) - E(T_1)]$. $(D')^{1/3} = (hcD/g^2\beta^2)^{1/3}$ (cm^{-1}). The numbering of the points corresponds to that of the compounds listed in Table I.

more effectively decreases D. The change in D from that of biphenyl is not doubled in going from one hydroxyl group ($\Delta D = 0.0052$ cm^{-1}) to two ($\Delta D = 0.0073$ cm^{-1}). The possibility of the requisite donation of electron density onto the ring is thus reduced for the second substituent by the presence of the first.

It is particularly interesting to note that although a CF_3 group might be expected to behave similarly to an F substituent, D for 4,4′-difluorobiphenyl is greater than that for biphenyl, unlike all other substituents studied here, whereas D for 4,4′-bis(trifluoromethyl)-biphenyl is slightly less than D for biphenyl.

Several spectra showed extra peaks or shoulders on existing peaks, notably 4,4′-diethyl-, 4,4′-diisopropyl-, 4,4′-di-*sec*-butyl-, and 4,4′-di-*tert*-butylbiphenyl (Figure 2A–D). For 4,4′-di-*tert*-butylbiphenyl dissolved in EPA, 2-methyltetrahydrofuran, 3-methylpentane, diethyl ether, and ethanol, peaks for two discrete sites are fully resolved (Figure 2B). In all glasses the two sites gave four peaks in the x,y region of the spectrum with approximately the same intensity ratios. There was no evidence of a concentration dependence of intensities in a study in EPA. The values of D are the same for both sites, but E for the less populated one was smaller in magnitude by 0.0040 cm^{-1}. In an effort to elucidate the origin of the anomalous peaks, a variable-temperature study of 4,4′-di-*tert*-butylbiphenyl in diethyl ether was performed. Over the range −196 to −170°, where the signal disappeared due to glass softening, no change was observed in field positions or relative intensity ratios. In cyclohexane, which powders instead of glassing upon freezing, one site occurred. D and E were calculated to be 0.1083 and −0.0046 cm^{-1}, respectively, differing from parameters for either glassy site.

Line widths in the spectra of 4,4′-bis(trideuteriomethyl)biphenyl-, 4,4′-dimethyl-, and 4,4′-bis(trifluoromethyl)biphenyl increased appreciably in the order listed (19.2, 29.5, 37–56 G, respectively). For the first two compounds, all lines were essentially the same width. For the latter, each pair of lines corresponding to the three canonical orientations was different.

Molecular Orbital Calculations. The theoretical framework for calculating D and E from molecular π-electron wave functions has been previously worked out (ref 25, and references therein). As a means of comparing the substituent effects on T_1 of substituted biphenyl with those on the corresponding anion radicals, D and E have been evaluated using the MO's generated through study of anion radicals and eq 9.37–9.39 of ref 25. These MO's gave the best fit between experimental and calculated results for epr spectra of radical anions, uv energies, and polarographic half-wave potentials of the molecules studied.[11,12,26] Since in the 4- and 4,4′-substituted biphenyls HOMO − 1 and LUMO + 1 are doubly degenerate, no attempt was made in the present investigation to include any triplet state configuration other than the HOMO → LUMO case. Interatomic distances and angles were based on the assumption of regular hexagonal coplanar rings having carbon–carbon bond distances of 1.40 Å.

The calculated values for D from MO theory for biphenyl, 4,4-dialkyl-, 4,4′-bis(trimethylsilyl)-, 4,4′-bis(trimethylgermyl)-, 4-trimethylsilyl-, and 4-trimethylgermylbiphenyl are all found to be 65–70% of the experimental values. For instance, for the dimethyl derivative, the values for D and E are 0.0733 and −0.690 cm^{-1}, respectively. The trend in substituent effect is reproduced, and thus the trends for the radical anions and first excited triplet states of substituted biphenyls seem to be similar.

It is interesting to note that D and E calculated from an SCF–CI treatment of biphenyl itself[27] were in substantial disagreement with experiment, although the same calculational method gave D and E for benzene and cata-condensed hydrocarbons which closely approached experimental results.

Discussion

In comparing the 4,4′-dialkylbiphenyls with biphenyl itself the decrease in D is consistent with an increase in the average separation between the unpaired spins. Since the z-axis distribution remains essentially constant through a series of similar molecules, this effect can be explained by delocalization of the triplet spin density onto the substituent either by a conjugative or by a spin polarization mechanism. The dependence of τ_p^0 on substituent is also explained by spin delocalization. The triplet state results by themselves do not allow a choice between the above pathways. A most significant result, however, is that no net differences are observed in the triplet state properties of the alkyl-substituted biphenyls, either by epr or by phosphorescence spectroscopy. This conclusion is similar to that obtained by uv spectroscopic and polarographic studies.[11] Electron spin resonance studies of the anion radicals of the same molecules also showed no substantial differences in ring proton coupling constants for the various substituents.[11]

---

(25) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(26) L. W. Bush, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1967.

(27) Y. Gondo and A. H. Maki, *J. Chem. Phys.*, 50, 3270 (1969).

The ZFS parameters of 4,4′-di-*tert*-butylbiphenyl, 4,4′-bis(trimethylsilyl)biphenyl, and 4,4′-bis(trimethylgermyl)biphenyl indicate that the average separation between unpaired electrons increases in the order C $\approx$ Ge $<$ Si. Thus, the net spin delocalization for the C and Ge substituents are about the same. Silicon is substantially better able to delocalize the triplet spins, results consistent with previous research showing that silicon is a better (p–d)π-bonding substituent than germanium when attached to aromatic systems.[12,28] As anticipated for a (p–d)π-bonding extension of the electron distribution, the effect of one trimethylmetal group on both D and the $S_0 \rightarrow T_1$ energy is half the effect of two groups within experimental error. If an inductive effect were operating to change the electron spin distribution, it might be expected that the presence of the first group would inhibit an equal change on the addition of the second group.

In studies of equilibria and reaction rates, the hydroxyl group is a better electron donor than the methoxy group when attached to an aromatic system.[6] In order for triplet state spin density to appear on either of these substituents, it is necessary that electron donation from the substituent to the ring occur. The result $D(\mathrm{OH}) < D(\mathrm{OCH_3})$ is consistent with hydroxyl group donation also being more facile in the triplet state.

A linear plot of ΔD *vs.* σ_p is obtained for the six disubstituted compounds containing the normally π electron-donating substituents, OCH_3, OH, and alkyls. ($\Delta D = D[\mathrm{Y(C_6H_4)_2Y}] - D[\mathrm{(C_6H_5)_2}]$ and σ_p is a Hammett parameter[6].) The least-squares line is described by

$$\Delta D = 0.020(\pm 0.002)\sigma_p - 0.0002(\pm 0.0005)$$

Although the parent biphenyl was not included in the least-squares analysis, it is important to note that within the probable error limits, the intercept is zero, the expected point for biphenyl. A similar linear relationship was reported for 1- and 2-substituted naphthalenes.[9]

The CF_3 group and the fluoro substituent might be expected to act similarly, behaving as strong electron acceptors, but this does not appear to be the case for substitution on the biphenyl nucleus. Fluorine is the only substituent examined here which increases D above that of the parent biphenyl (Table I). No rationalization has been offered for either this increase or the essentially zero value of E (0.0 from this work; 0.0006 cm^{-1} from magnetophotoselection[24]). On the other hand, CF_3 substitution causes a small decrease in D, possibly due to a π-inductive effect which rearranges spin in the biphenyl nucleus without putting substantial spin density onto the π substituent.[29] However, the line-width variation among the CD_3, CH_3, and CF_3 derivatives can be attributed to differences in hyperfine interaction between the unpaired spins and the substituent nuclei, thus indicating some spin density on the CF_3 substituent.

Other observations verify the difference between F- and CF_3-substituted biphenyls. The $E(S_0 \rightarrow S_1)$ is much larger for difluorobiphenyl[30] than for biphenyl but is slightly smaller for 4,4′-bis(trifluoromethyl)biphenyl than for the parent. The $T_1 \rightarrow S_0$ emission for 4,4′-bis(trifluoromethyl)biphenyl is of higher energy than the corresponding transition for the parent or fluorine derivative (Table I). A purely inductive mechanism cannot be invoked to explain the triplet state and other spectroscopic results for *both* the fluorine and trifluoromethyl derivatives.

It is interesting to note that a plot of $D^{1/3}$ *vs.* $[E(S_1) - E(T_1)]$, the difference in energy between the first excited singlet and triplet states (Figure 3), is approximately linear with the exception of the CF_3 compound. This linearity is anticipated since $D^{1/3}$ $(\propto \langle 1/r_{12}^3\rangle^{1/3})$ is a measure of the average inverse separation between the unpaired electrons,[17] whereas the lowering of T_1 with respect to S_1 is proportional to the expectation value $\langle 1/r_{12}\rangle$.

The appearance of shoulders and extra peaks in the spectra of the 4,4′-dialkylbiphenyls (excluding the methyl derivative) can be explained in terms of environmental effects.[31] In EPA glass, it appears that as the steric requirements of the substituent increase from ethyl to *tert*-butyl, the solvent matrix is less able to randomly solvate the molecule and the shoulder found for diethylbiphenyl increases through the series until two definite peaks are resolved for di-*tert*-butylbiphenyl in two discrete sites in the glass.

Our epr and phosphorescence data suggest that the triplet state energy and spin distribution for biphenyl are altered by substituents through delocalization of charge and/or spin. In particular, these effects are greatest where opportunity for (p–d)π delocalization exists or when the substituents are strong electron withdrawing groups. As also found for the anion radicals, no significant differences in triplet state properties are observed among the alkylbiphenyls.

Acknowledgments. H. V. T. expresses appreciation for a predoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service. This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center, and in part by the Petroleum Research Fund, administered by the American Chemical Society. H. V. T. also thanks George Lozos and Roger Crain for their help in obtaining the triplet state esr spectra.

---

(28) M. D. Curtis, R. K. Lee, and A. L. Allred, *J. Amer. Chem. Soc.*, **89**, 5150 (1967).

(29) D. Holtz, *Chem. Rev.*, **71**, 139 (1971).

(30) A. L. Allred and L. W. Bush, *Tetrahedron*, **24**, 6883 (1968).

(31) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1663 (1964).