into ice, no precipitate was produced. Evaporation of the solution to near dryness produced white crystals which were diluted with water and filtered producing 0.2 g (67%) of product, mp 142–146°. The infrared spectrum was identical with that of di(methylsulfonyl)methane.

Registry No.—Carbon disulfide, 75-15-0; **1**, 26958-44-1; **4a**, 26958-45-2; **4b**, 26958-46-3; **4c**, 26958-47-4; **6**, 26958-48-5.

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Solvent Effects on the Energy of the Principal Electronic Transition of *p*-Nitrotoluene-α-d_3 and *p*-Methylanisole-α-d_3

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In recent years it has been postulated that the experimental finding that is called the Baker–Nathan effect owes its origin to direct solvent influences rather than to an inherent predominance of C–H hyperconjugation, other modes of electronic stabilization such as C–C hyperconjugation, and the inductive effect. One group has attributed the Baker–Nathan effect to steric hindrance to solvation near bulkier alkyl groups.[1,2] Another has attributed it to solvent enhancement of C–H over C–C hyperconjugation, through incipient hydrogen bonding of the α hydrogens of the alkyl substituent with the solvent.[3] The observation that the inductive order of principal electronic transition energies found for *p*-alkyl nitrobenzenes and acetophenones in the gas phase and in inert solvents tends to be inverted in basic solvents is qualitatively consistent with either viewpoint.[2,4] It therefore appeared desirable to try to find direct evidence for solvent enhancement of C–H hyperconjugation in the effect of a number of solvents on the relative principal electronic transition energies of *p*-nitrotoluene and *p*-nitrotoluene-α-d_3. The principal electronic transition of the nitrobenzenes is highly electronic demanding on the para substituent, the electron migration being in the long axis of the molecule and away from the substituent.[5] Also included here are solvent studies on the energy of the principal electron transition of *p*-methylanisole and *p*-methylanisole-α-d_3, in which the electron migration is toward the substituent.[5]

An increase in excitation energy spread between *p*-nitrotoluene and *p*-nitrotoluene-α-d_3 in basic solvents could be considered as direct evidence for solvent enhancement of C–H hyperconjugation. On the other hand, the absence of such a finding does not prove that solvent enhancement of C–H hyperconjugation is absent in other systems, *e.g.*, in chemical transitions. That is, in the present system, in contrast to chemical systems, the upper (electronic) state that originally arises is not an "equilibrium state." In the short time of the electronic excitation of a molecule (*ca.* 10^{-16} sec), nuclear relaxation (*ca.* 10^{-13} sec) is minimal (Franck–Condon principle). Thus, orientation of basic portions of solvent molecules to the α hydrogens of the polar excited state species may be minimal, since such orientation is essentially that pertaining in ground state species.

The only trend discernible is a slight increase in $\nu_{CD_3} - \nu_{CH_3}$ in highly acidic solvents, a trend that accompanies a large increase in $\nu_H - \nu_{CH_3}$, the excitation energy difference between nitrobenzene and *p*-nitrotoluene (Table I). In fact, a plot of $\nu_H - \nu_{CD_3}$ against $\nu_H - \nu_{CH_3}$ is linear to a high degree of precision. This indicates that in the transition to the nonequilibrium Franck–Condon excited state, differential solvent perturbation of the CH_3 and CD_3 groups is negligible. The slope of the line is 1.036 with a standard deviation of ± 0.002 and a correlation coefficient of 0.999^+. In terms of the Hammett relationship, the slope is the substituent constant ratio, $\sigma_{CH_3}/\sigma_{CD_3}$,[6] and the value of the slope can be taken as meaning that the methyl group has a greater absolute σ value than the CD_3 group.[8]

TABLE I

VALUES OF ν_H, $\nu_H - \nu_{CH_3}$, AND $\nu_{CD_3} - \nu_{CH_3}$ IN CM^{-1} FOR *p*-$RC_6H_4NO_2$ IN VARIOUS SOLVENTS[a–c]

Solvent	ν_H	$\nu_H - \nu_{CH_3}$	$\nu_{CD_3} - \nu_{CH_3}$
Gas phase	41,820	1850	80[d]
Heptane	39,700	1810	50
n-$BuNH_2$	38,200	1920	40
tert-BuOH	38,790	1960	40
Dioxane	38,650	2090	30
EtOH	38,530	2090	30
H_2O	37,440	2280	50
52% $HClO_4$	36,810	2480	60
70% $HClO_4$	35,720	2750	70
96% H_2SO_4	34,580	2710	70

[a] Values of ν_{max}, determined as previously described,[5] are averages of three determinations, duplicable to ±15 cm^{-1} or better except where noted. [b] Compound preparation and purification also previously described.[5] [c] The isotopic composition of the sample of *p*-nitrotoluene-α-d_3 was: d_3, 85.4%; d_2, 13.9%; d_1, 0.7%; d_0, 0%.[5] [d] Value of ref 5, duplicable to ±20–30 cm^{-1}.

The effect of a few solvents on the excitation energy of *p*-methylanisole-α-d_3 is shown in Table II. Within

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(1) W. M. Schubert and D. F. Gurka, *J. Amer. Chem. Soc.*, **91**, 1443 (1969), and preceding papers.

(2) W. M. Schubert, J. Robins, and J. Haun, *ibid.*, **79**, 910 (1957).

(3) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957); V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(4) A quantitative treatment of the data in twelve widely varying solvents, dealing with the relative linearity of plots of $\nu_H - \nu_R$ against ν_H was considered to favor the steric hindrance to solvation argument.[2]

(5) W. M. Schubert, R. B. Murphy, and J. Robins, *J. Org. Chem.*, **35**, 951 (1970), and references therein.

(6) Since ν is proportional to energy, the Hammett relationship for electronic transitions can be written $\nu_H - \nu_{CH_3} = \sigma_{CH_3}\rho'$, where ρ' is dependent on the solvent and the units of energy used.[7] By combining this equation with the corresponding one for CD_3 one obtains $\nu_H - \nu_{CH_3} = (\sigma_{CH_3}/\sigma_{CD_3})(\nu_H - \nu_{CD_3})$, which is the equation of the line.

(7) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(8) It is to be noted that the various kinds of σ values that have been assigned to alkyl substituents, all negative, have the wrong sign for the principal electron transition of anisoles, phenols, and anilines.[5,9]

(9) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962).

TABLE II

VALUES OF ν_H, $\nu_H - \nu_{CH_3}$, AND $\nu_{CD_3} - \nu_{CH_3}$ IN CM^{-1} FOR p-$RC_6H_4OCH_3$ IN VARIOUS SOLVENTS[a-c]

Solvent	ν_H	$\nu_H - \nu_{CH_3}$	$\nu_{CD_3} - \nu_{CH}$
Gas phase	46,510	1010	130[d]
Heptane	45,530	1090	80
MeCN	45,530	770	80
Dioxane	45,350	730	80
EtOH	45,570	860	80
H_2O	46,180	910	100

[a] Values of ν_{max}, determined as previously described,[5] are averages of two determinations, duplicable to ±20 cm^{-1} except where noted. [b] Compound preparation and purification also previously described.[5] [c] The isotopic composition of the sample of *p*-methylanisole-α-d_3 was: d_3, 85.0%; d_2, 9.8%; d_1, 0.7%; d_0, 4.5%.[5] [d] Value of ref 5, duplicable to ±20–30 cm^{-1}.

experimental error no solvent effect on $\nu_{CD_3} - \nu_{CH_3}$ is discernible. The interesting fact that *p*-alkyl lowers the principal electronic excitation energy of anisole and similar compounds,[8] and that both for compounds of the anisole type and nitrobenzene, *p*-CD_3 derivatives have a slightly higher excitation energy than the *p*-CH_3 derivatives, has been commented upon previously.[5,9]

Although base solvation of *p*-CH_3 is indetectable in this particular system, the pronounced lowering of the excitation energy of each nitrobenzene as solvent acidity is increased[10] indicates that acidic hydrogen bond solvation of the nitro oxygens is highly important in the total solvent effect.[2] The *increase* in excitation energy of the anisoles in proceeding from heptane to water solvent is attributable to acidic hydrogen bond solvation of the ether oxygen.[5]

Registry No.—*p*-Nitrotoluene-α-d_3, 23346-24-9; *p*-methylanisole-α-d_3, 23346-26-1.

Acknowledgment.—Financial support by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(10) For nitrobenzene itself, the excitation energy is 14.6 kcal mol^{-1} less in 96% sulfuric acid than in heptane.

Protonation and Methylation of Dianions Derived from 1,4-Bisbiphenylenebutatriene and 1,4-Bisbiphenylene-1,3-butadiene

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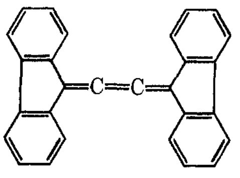
It was the purpose of this investigation to extend our knowledge of the chemical reactions of the dianions generated from aryl-substituted butatrienes. The chemical reactivity of the dianion derived from tetraphenylbutatriene has been the subject of several papers.[1]

The butatriene chosen for the present study was 1,4-bisbiphenylenebutatriene (II). It is a planar molecule

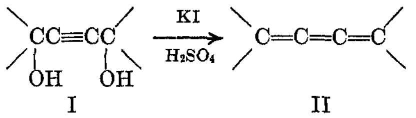


II

and extensive resonance delocalization is possible. This fact is clearly indicated by the colors of tetraphenylbutatriene and 1,4-bisbiphenylenebutatriene. The first is bright yellow and absorbs in the visible at 408 mμ, whereas the second is deep red with a visible absorption at 483 mμ. Due to some steric inhibition of resonance, delocalization is less in the first compound.

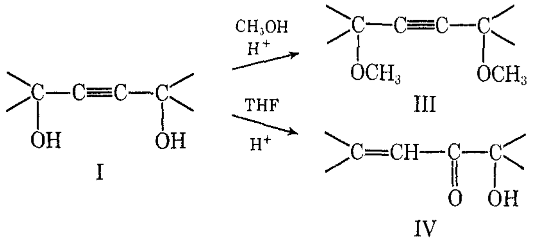
1,4-Bisbiphenylenebutatriene was prepared from 1,4-bisbiphenylene-2-butyne-1,4-diol by the potassium iodide–sulfuric acid method described by Wolinski[2] (Scheme I).

SCHEME I



The dimethyl ether of I was readily prepared by treating the diol with methanol and sulfuric acid. The yellow color produced during the reaction was due to the formation of a small amount of 1,4-bisbiphenylene-1-buten-3-one-4-ol. The latter was formed as the result of an allylic-type rearrangement followed by a tautomeric shift to a keto structure. The keto alcohol was the main product when tetrahydrofuran was used in place of methanol (Scheme II).

SCHEME II



The hybrid dianion, $[\mathrm{C}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{=}\mathrm{C}\overset{\cdots}{-}\mathrm{C}]^{2-}$ may be obtained directly from 1,4-bisbiphenylenebutatriene by treatment with sodium–potassium alloy but it is more readily prepared by treating the dimethyl ether III with sodium–potassium alloy.

Protonation of the dianion was first accomplished by the addition of methanol. The protonation was slow as evidenced by the very slow decolorization of the dianion solution. Only 1,4-bisbiphenylene-1,3-butadiene (V) was obtained from this reaction. When acetic acid was used as the protonating agent, decolorization occurred almost at once. In addition to the 1,3-diene V, 1,4-bisbiphenylene-2-butyne (VI) was isolated (Scheme III).

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[1] (a) A. Zweig and A. Hoffman, *J. Amer. Chem. Soc.*, **84**, 3278 (1962); (b) R. Nahon and A. R. Day, *J. Org. Chem.*, **30**, 1973 (1965); (c) S. Sisenwine and A. R. Day, *ibid.*, **32**, 1770 (1967).

[2] J. Wolinski, *Rocz. Chem.*, **29**, 23 (1955).