It is felt that the analysis has been carried as far as it can be reasonably expected. Any conclusion based on further subtleties would be unreliable since the purity of the investigated material was only 80%. Further refinements in the parameters might be compensated by changing the concentration or structure of the diindenylcobalt contribution. Up to this point, however, the parameters in their limits are little affected by the model chosen for the 10% diindenylcobalt model.

Discussion

Two results were brought about by this investigation. First, information was obtained concerning the structure of the indenyl free radical. Though the more sophisticated second model described above does not represent a unique solution as far as the absolute values of its parameters are concerned, it establishes some likely structural features for indenyl. Thus, the data indicate that the molecule is constructed from a set of distinctly different C–C bonds. Their average is in good agreement with HMO calculations. In addition the experiment favors the assumption that some of the C–C bonds deviate more from the average than is predicted by HMO calculations.

Secondly, this study proves that the method of electron diffraction may be successfully applied to the investigation of highly unstable compounds. The procedure to be followed consists in the production of the desired molecules as close to the electron beam as is possible. As far as pyrolysis of the parent molecule is involved, a considerable improvement of the experimental technique used in the investigation at hand may be expected. Thus, uncertainties were introduced into the results of this work by the presence of undissociated starting material. This disadvantage might be removed by recording the ED patterns at different temperatures in order to find the optimal experimental conditions. As a valuable by-product, thermodynamic data might be obtained, as has already been done for another case recently studied in this laboratory.[23]

As a useful tool in such an investigation, a high-temperature nozzle has been designed, having a heated filament which makes it possible to obtain temperatures up to 1000°. With this, work has been started in an attempt to produce cyclobutadiene (C_4H_4), cyclopentadienyl (C_5H_5), cycloheptatrienyl (C_7H_7), and fluorenyl ($C_{13}H_9$), as well as a variety of other similar compounds.

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(23) L. S. Su and R. A. Bonham, personal communications.

Anodic Oxidation Pathways of Substituted Triphenylamines. II. Quantitative Studies of Benzidine Formation

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Abstract: A previous study concerned a general, qualitative picture of the anodic oxidation of triphenylamines in acetonitrile leading to substituted benzidines as products. The rates of the benzidine coupling reactions now have been measured. Marked substituent effects on these rates are shown to be qualitatively consistent with simple HMO reactivity parameters. A fairly complete picture of the anodic oxidation pathways of substituted triphenylamines is presented.

A previous study developed a general, qualitative picture of the behavior of substituted triphenylamines upon anodic oxidation in acetonitrile.[2] Two extremes in the oxidation pathways were noted. If the triphenylamine was completely *para* substituted, stable monocation radicals were obtained which could be completely characterized by the electrochemistry and electron paramagnetic resonance (epr) spectra. At the other extreme, with completely unsubstituted triphenylamine, the initial cation radical rapidly coupled to form the tetraphenylbenzidine which subsequently underwent further oxidation. The general scheme of this process is adequately described in part I. A few partially *para*-substituted triphenylamines were studied and *p*-benzidine formation was indicated but not unequivocally proven in all cases.

The present results have extended the initial studies to show that *p*-benzidine formation is the predominant coupling reaction. Furthermore, the marked substituent effects on the rates of benzidine formation

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(1) Author to whom correspondence should be addressed.

(2) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, 88, 3498 (1966), referred to herein as part I.

Table I. Electrochemical Characteristics of Tri-*para*-Substituted Triphenylamines, $R_1R_2R_3N$

No.	R_1	R_2	R_3	$E_{p/2}$[a]	$i_p/V^{1/2}C$[b]	$it^{1/2}/C$[c]	$i\tau^{1/2}/C$[d]
I	C_6H_4OMe	C_6H_4OMe	C_6H_4OMe	0.52	28.0	45.5	73.0
II	C_6H_4Me	C_6H_4Me	C_6H_4Me	0.75	29.4	49.0	76.0
III	C_6H_4F	C_6H_4F	C_6H_4F	0.95	28.5	51.0	84.0
IV	C_6H_4Cl	C_6H_4Cl	C_6H_4Cl	1.04	30.5	52.5	81.5
V	C_6H_4Br	C_6H_4Br	C_6H_4Br	1.05	30.0	49.5	79.5
VI	C_6H_4COOMe	C_6H_4COOMe	C_6H_4COOMe	1.26	26.5	45.0	71.5
VII	C_6H_4OMe	C_6H_4OMe	$C_6H_4NO_2$	0.86	27.2	46.0	72.5
VIII	C_6H_4Me	C_6H_4Me	$C_6H_4NO_2$	1.03	27.0	48.0	75.5
IX	$C_6H_4NO_2$	$C_6H_4NO_3$	$C_6H_4NO_2$[e]				

[a] In volts *vs.* sce. [b] i_p = peak current, V = scan rate (1.25 to 16.7 V/min). [c] From chronoamperometric measurements. [d] From chronopotentiometric measurements. [e] No solvent could be found to dissolve this compound.

which were noted previously have been evaluated quantitatively and shown to be consistent with reactivity parameters from simple HMO calculations. A fairly complete and general picture of the anodic oxidation pathways of triphenylamines can be given now and is summarized briefly herein.

Experimental Section

The experimental techniques were, in general, identical with those of part I. The rates of the coupling reactions were measured by the standard potentiostatic (chronoamperometric) technique developed by Alberts and Shain.[3] Using potentiostatic control at a planar, platinum electrode, a given triphenylamine (TPA) was oxidized and its current-time curve followed for a few seconds. The recorded output was to a fast pen-and-ink recorder or an oscilloscope depending on the time interval. If no chemical coupling occurs, the current-time curve is proportional to n_1 electrons for the primary TPA oxidation. If the benzidene coupling rate is infinitely fast, the current-time curve corresponds to $(n_1 + n_2)$ electrons. For intermediate values of the coupling rate constant, the current-time curve varies between the above limits and can be evaluated. The rate constants were calculated *via* a solution of the digital simulation methods of Feldberg[4-6] for a second-order reaction. Details of the calculations, completely similar in practice to the well-established first-order rate constant calculations,[3-5] will soon be available[6] and are not detailed here. For the present purposes it is sufficient to note that reproducible rate constants which were consistent only with a bimolecular coupling reaction were obtained. Only the relative rates as a function of substituents are of interest, and the experimental details of the measurements do not affect any of the conclusions of the work. (The coupling rates were also measured by a rotated disk technique for an independent cross-check. Excellent agreement was obtained.) All further details of the experimental procedures are given in part I unless they are necessary for the discussion herein.

Many of the substituted triphenylamines were prepared and several of them are apparently new compounds in the literature. Although their preparations and purifications followed relatively straightforward techniques, the pertinent data and their analyses are recorded in the Appendix for future reference. For convenience, the compounds are given Roman numeral designations in order of their appearance in various tables.

Results and Discussion

The object of the present work was to examine the behavior of a wide series of triphenylamines, starting with the tri-*para*-substituted compounds and selectively removing substituents and moving them to *ortho* and *meta* postions. Hence the results are summarized in this fashion, starting with the tri-*para*-substituted compounds.

A. *para*-Substituted Triphenylamines. As shown in part I, all of the tri-*para*-substituted triphenylamines give very stable monocation radicals. The tri-*para*-anisylamine is a prime example of this series where the monocation is extremely stable even in acetone-water buffer systems from pH 2 to 6. The quantitative electrochemical characteristics of a series of tri-*para*-substituted compounds are given in Table I. The characteristic ratios $i_p/V^{1/2}C$, $it^{1/2}/C$, and $i\tau^{1/2}/C$ for peak voltammetry, chronoamperometry, and chronopotentiometry, respectively, are all characteristic of a simple one-electron process with no chemical complications. The epr spectra of the monocation radicals found in this oxidation are consistent with this interpretation and have been discussed previously.[2] All of the tri-*para*-substituted derivatives gave a second stage of oxidation which is, in general, irreversible and leads to products which have not been characterized. Unless otherwise noted, all of the electrochemical characteristics referred to herein pertain only to the initial one-electron transfer (*i.e.*, to the first oxidation peak or wave).

Table II. Electrochemical Characteristics of Di-*para*-substituted Triphenylamines, R_1R_2PhN

No.	R_1	R_2	$E_{p/2}$[a]	k[b]
X	C_6H_4OMe	C_6H_4OMe	0.63	Very slow
XI	C_6H_4Me	C_6H_5Me	0.82	$1.60 \pm 0.32 \times 10^1$
XII	C_6H_4Cl	C_6H_4Cl	1.01	$4.02 \pm 0.31 \times 10^2$
XIII	$C_6H_4NO_2$	$C_6H_4NO_2$	1.36	10^4–10^5
XIV	C_6H_4OMe	$C_6H_4NO_2$	0.98	$1.50 \pm 0.3 \times 10^1$

[a] In volts *vs.* sce, measured at a scan rate of 16.7 V/min. [b] Bimolecular rate constant in l. mole^{-1} sec^{-1}; concentration of amine 2m*M* in all cases; solvent, acetonitrile–0.10 *M* TEAP. Only approximate values of *k* evaluated; see Table III for precise data.

As *para* substituents are removed from the phenyl rings, there are very pronounced changes in the reactivity of the monocations to couple and form benzidines. These reactivity differences are not due simply to unblocking of the *para* coupling sites but are clearly due to substituent effects. As a measure of the reactivity, one can examine the variation in the bimolecular rate constant for the benzidine coupling reaction. This is seen in Table II for a few di-*para*-substituted triphenylamines. Here the rate constant, *k*, for dimerization to the benzidine was only measured approximately. (The substituent effect is more effectively seen in the mono-*para*-substituted compounds. Accurate rate constants were evaluated for these compounds as shown later.) Nevertheless, the substituent effect is very evident. Thus, the di-*p*-methoxy derivative, with one open position for *p*-benzidine formation, is very stable as the monocation, and the

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(3) G. S. Alberts and I. Shain, *J. Am. Chem. Soc.*, **35**, 1859 (1963).

(4) S. W. Feldberg and C. Aurbach, *ibid.*, **36**, 505 (1964).

(5) M. D. Hawley and S. W. Feldberg, *J. Phys. Chem.*, **70**, 3495 (1966).

(6) S. W. Feldberg in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., in press.

bimolecular rate constant is too slow to even measure. The dimethyl compounds also give a relatively stable monocation, but the dichloro cation shows fairly extensive coupling. The dinitro derivative, with only the same statistical chance for coupling as the dimethoxy compound, couples at a tremendously enhanced rate. Finally, the considerable stabilizing influence of a single *p*-methoxy substituent is seen in compound XIV where the influence of the methoxy "overshadows" that of the nitro, and the coupling rate is quite slow.

Although the cyclic voltammetry of these systems indicates clearly the benzidine coupling reaction, it is necessary to provide independent, auxiliary data to verify this reaction. The expected *p*-benzidine from compound XI (N,N,N′,N′-tetra-*p*-tolylbenzidine) was prepared by chemical means as an authentic sample. Solutions of it and the parent di-*p*-methyltriphenylamine (XI) were oxidized *in situ* in a Cary spectrophotometer. A platinum gauze and miniature calomel electrode inserted directly in the cuvette allowed spectra to be obtained following a short period of electrolysis (*i.e.*, within the time scale of ordinary voltammetry). Figure 1 illustrates the optical spectra of the resulting electro-oxidized solutions. Curve B is that from the *p*-benzidine, and the absorption at 475 mμ is that due to the benzidine cation. Upon oxidation of the parent triphenylamine, one obtains a large absorption at 668 mμ characteristic of the triphenylamine cation. However there also is present an appreciable amount of the benzidine spectrum (λ_{max} 475 mμ) resulting from the coupling reaction. Because of difficulty in preparing and purifying all of the benzidines, it was not feasible to prove *p*-benzidine formation for each of the individual triphenylamines. Further examples are given in the next section, and there remains no doubt that the *p*-benzidine formation is at least the *major* chemical follow-up reaction in the electrooxidation of the triphenylamines under the present conditions.

Precise coupling rates were measured for the mono-*para*-substituted compounds shown in Table III. It should be further noted that the evaluated rate constants fit the working curves for a bimolecular dimerization model as required by the benzidine coupling process.

Table III. Coupling Rates of Mono-*para*-substituted Triphenylamines, R_1Ph_2N

No.	R	$E_{p/2}$[a]	Potentiostatic k[b]
XV	C_6H_4OMe	0.76	*Ca.* 1.0[c]
XVI	C_6H_4Ph	0.89	$4.63 \pm 0.6 \times 10^1$
XVII	C_6H_4Me	0.88	$1.46 \pm 0.12 \times 10^2$
XVIII	C_6H_4Cl	0.99	$9.6 \pm 0.5 \times 10^2$
	Triphenylamine	. . .	$2.4 \pm 0.5 \times 10^3$
XIX	C_6H_4CN	1.14	$6.8 \pm 1.2 \times 10^3$
XX	$C_6H_4NO_2$	1.17	$1.3 \pm 0.1 \times 10^4$

[a] In volts *vs.* sce, measured at a scan rate of 16.7 V/min. [b] Bimolecular rate constant in l. mole^{-1} sec^{-1}; concentration of triphenylamines was varied from 1.0×10^{-4} to 2.0×10^{-3} *M*; solvent, acetonitrile–0.1 *M* TEAP in all cases. [c] Difficult to measure accurately by electrochemical techniques owing to slowness.

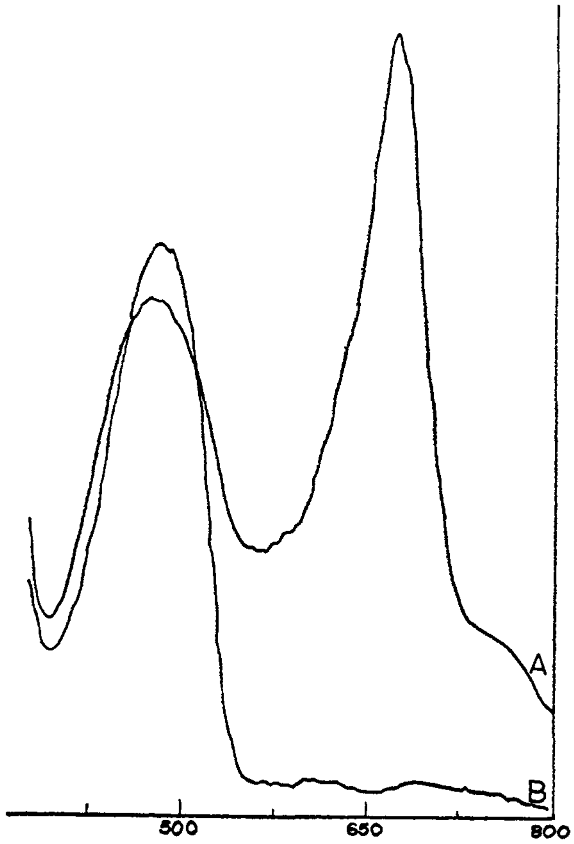
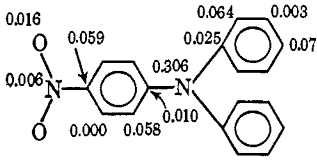


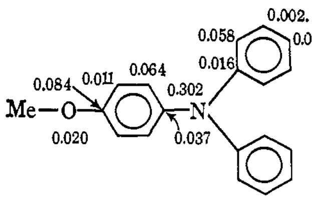
Figure 1. Visible absorption spectra generated at constant current in acetonitrile: (A) 4,4′-dimethyltriphenylamine, (B) N,N,N′,N′-tetra-*p*-tolylbenzidine. Abscissa is wavelength in mμ.

With only one *para* substituent, the effects are clearly seen. Triphenylamine itself is included in Table III for comparison. The extreme stabilizing effect on the monocation is seen in the methoxy derivative and to a lesser extent in the phenyl and methyl compounds (XV, XVI, and XVII, respectively). On the other hand, the strong enhancement of benzidine coupling is clear with the cyano and especially the nitro derivative (compounds XIX and XX.)

If one takes the reasonable approach that a high unpaired electron density in the *para* positions of the unsubstituted phenyl groups of the monocation radical provides an easy access for the benzidine coupling reaction, simple HMO calculations for the mononitro derivative (cation radical) are in accord with the enhanced rate. Thus, the unpaired electron density (c^2 values) in the nitro cation radical is as seen below (only one of the unsubstituted phenyl rings is labeled). It is clear that the nitro cation has an appreciable unpaired electron density in the *ortho* and *para* positions of the unsubstituted phenyl groups. This



4-nitrotriphenylamine



4-methoxytriphenylamine

Table IV. Electrochemical Characteristics of *ortho*-Substituted Triphenylamines, $R_1R_2R_3N$[a]

No.	R_1	R_2	R_3	$E_{p/2}$[b]	k[c]
Mono-*ortho*-Substituted					
XXI	C_6H_5	C_6H_5	C_6H_4OMe	0.96	$>10^3$
XXII	C_6H_5	C_6H_5	C_6H_4Me	1.02	$>10^3$
XXIII	C_6H_5	C_6H_5	C_6H_4Cl	1.08	$\gg 10^3$
Tri-*ortho*-Substituted					
XXIV	C_6H_4OMe	C_6H_4OMe	C_6H_4OMe	0.80	$6.0 \pm 0.5 \times 10^1$
XXV	C_6H_4Me	C_6H_4Me	C_6H_4Me	1.01	$1.90 \pm 0.15 \times 10^2$
XXVI	C_6H_4Cl	C_6H_4Cl	C_6H_4Cl	1.44	$5.50 \pm 0.60 \times 10^2$

[a] Substituents are *ortho* to amine N. [b] In volts *vs.* SCE, measured at a scan rate of 16.7 V/min. [c] Bimolecular rate constant, l. mole^{-1} sec^{-1}; concentration of amine = 2 mM in all cases; solvent was acetonitrile–0.10 M TEAP.

density is, in fact, slightly greater than for triphenylamine itself, and hence one could predict an enhanced coupling rate for the nitro and cyano derivatives. At the opposite extreme is the *p*-methoxy derivative, with less unpaired density in the possible coupling positions. The HMO unpaired electron densities of the cations of the phenyl, methyl, and chloro derivatives are intermediate, and the qualitative trend is in line with that of the measured coupling rates. These HMO calculations are intended only for qualitative trends in reactivity and involve a choice of heteroatom parameters. No attempt was made to optimize these parameters. In general, values which had been used successfully for epr calculations were employed. These parameters are listed together with a brief explanation of their usage in the Appendix. No further quantitative significance should be attached to these calculations, but the predictions are in gratifying accord with the experimental observations.

Clearly, from the HMO calculations, one also has to admit that *o*-benzidine coupling reactions are possible. It is certainly to be expected that steric considerations would be less favorable for *ortho* coupling (as borne out by molecular models), but it cannot be eliminated. The mono-*para* derivatives were examined very closely and the experimental evidence presented below indicates that the *p*-benzidine is at least the predominant species formed.

For the mono-*p*-methyl compounds (XVII), both the cyclic voltammetry and *in situ* visible spectra of the parent and an authentic sample of the *p*-benzidine show matching characteristics. For the *p*-phenyl derivative (XVI), an exhaustive controlled-potential electrolysis was carried out at a potential slightly past the first oxidation peak. The solution resulting showed cyclic polarograms characteristic of a *p*-benzidine. This solution was then exhaustively reelectrolyzed at 0.0 V to reduce the fully oxidized benzidine expected to be in solution. The solution was chromatographed on alumina and extracted with benzine and a crystalline product was obtained (uncorrected mp 132–136°). The literature melting point of N,N′-dibiphenyl-N,N′-diphenylbenzidine is 135–140°.[7] It seems clear the *p*-benzidine was the major product in this case. For the nitro derivative XX, *in situ* electrolysis in the Cary spectrophotometer gives a common peak at 645 mμ (with a shoulder at 500 mμ) for both the triphenylamine and the authentic *p*-benzidine. Because of rapid coupling it is not possible to identify with certainty any absorption due to the primary cation radical.

In all these instances, although *ortho* coupling to the corresponding benzidines (as well as other modes of chemical reaction of the substituted triphenylamine cations) cannot be dismissed entirely, the experimental evidence seems ample that the *p*-benzidine pathway is the predominant one.

B. *ortho*-Substituted Triphenylamines. It was desirable to study the *ortho*-substituted triphenylamines because one now has open *para* positions for the benzidine coupling but at the same time has introduced steric complications due to added twisting of the substituted triphenylamine. By examining triphenylamines with only one *ortho* substituent, one can possibly see how twisting of one ring affects the follow-up chemical reactions. With all three rings *ortho* substituted one can study the *ortho*-substituent effects on a twisted but otherwise symmetrical molecule. The data are so subdivided in Table IV. Again rate constants for the coupling reaction were measured only qualitatively.

The first three mono-*ortho*-substituted compounds behave similarly, and the *o*-methoxy XXI can be taken as an example. All of the compounds couple rapidly (it will be shown below that again *p*-benzidine formation is the major reaction). In the case of the *o*-methoxy it may seem surprising to have a rapid coupling rate since it was previously shown that a *p*-methoxy seriously inhibited coupling. This apparent anomaly is readily explained by some simple HMO calculations. Thus if one compares the energy of the highest filled MO for 4-methoxytriphenylamine *vs.* 2-methoxytriphenylamine, assuming equivalent configurations for both species, one obtains the results in units of β: 4-OMe, $E_{HF} = -0.3454$; 2-OMe, $E_{HF} = -0.3488$. From such data one would anticipate the ease of oxidation and hence $E_{p/2}$ values to be almost identical. In fact, the 2-OMe derivative is *ca.* 0.2 V *more difficult* to oxidize ($E_{p/2}$ for 2-OMe is 0.96 V, Table IV, $E_{p/2}$ for 4-OMe is 0.76 V; see Table III). Such difficulty of oxidation is perfectly consistent with the *o*-methoxy derivative being twisted severely owing to steric crowding. Using the $E_{p/2}$ values to calculate the twist angle, as has been done by Geske and coworkers[8] and Bard,[9] leads to an estimate of the twist angle θ of *ca.* 45° (in this case relative to that of triphenylamine itself). It is recognized that the $E_{p/2}$ values used are incorrect by a small amount due to the presence of the fast follow-up chemical reaction, and thus the twist angle calculations are approximations. However, since

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(7) J. Piccard and F. de Montmollin, *Helv. Chim. Acta*, 6, 1011 (1923).

(8) D. H. Geske, J. L. Ragle, M. A. Bambenck, and A. L. Balch, *J. Am. Chem. Soc.*, 86, 987 (1964).

(9) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, 70, 404 (1966).

triphenylamine itself is already considerably twisted, it is evident the *ortho*-substituted derivatives will be considerably more so. Hence, the ring containing the methoxy substituent has a considerably diminished effect upon the rest of the π system. The result is that the unsubstituted phenyl rings have a substantial unpaired electron density at the *ortho* and *para* positions, and benzidine coupling is favorable. In fact, the coupling rates are faster than that of triphenylamine itself in accord with expectations. However, from the fact that the coupling rates do vary for the three mono-*ortho* compounds, the substituent effect is transmitted somewhat; *i.e.*, the substituted (twisted) ring is not totally decoupled from the remainder of the π system. If it were totally decoupled, all three compounds would have the same coupling rate.

For the tri-*ortho*-substituted derivatives (XXIV, XXV, and XXVI), it is difficult to put any calculational emphasis on the twisting. All three rings are obviously differently twisted than in triphenylamine itself. All *para* positions are open for coupling, and one could expect slower rates than for the triphenylamine and with the individual rates in the usual order of the substituent effect. This is seen to be the case and the coupling rates are quite low.

For the tri-*o*-methoxy compound it was possible to positively verify *p*-benzidine formation. With an authentic sample of the benzidine, the cyclic voltammetry matched that formed from the parent amine. As further proof, identical epr spectra are obtained after electrolysis of the tri-*o*-methoxytriphenylamine and the corresponding benzidine. In the former case initially the epr spectrum shows some initial cation radical which soon is replaced by that of the benzidine cation formed in the follow-up reaction. The benzidine of compound XXV was available and was likewise detected in the amine system. The benzidine was not available for checking compound XXVI, but the same mechanism seems to be present.

C. *meta*-Substituted Triphenylamines. Only three compounds in this series were prepared, but these were sufficient to provide some surprising results. The three compounds were

XVII	3-Methoxytriphenylamine	$E_{p/2} = 0.91$ V
XXVIII	Tri-*m*-anisylamine	$E_{p/2} = 0.92$ V
XXIX	Tris(*m*-nitrophenyl)amine	$E_{p/2} = 1.44$ V

The two methoxy compounds are similar in that the initial oxidation is irreversible and a fast follow-up reaction is indicated. However, instead of the coupling product being more easy to oxidize than the starting material (as is the case with a planar benzidine being formed), the coupling product with the *meta* compounds oxidized at about the same potential or more anodic than the starting compounds. This result would be reasonable if *p*-benzidines are again formed. With bulky substituents *ortho to the ring-ring bond* in the benzidine, it would be expected to be twisted and hence to be more difficult to oxidize than its planar analog.

Since a methoxy substituent in a *meta* position has an opposite effect to one in an *ortho* or *para* position, it is not suprising that compounds XVII and XVIII couple more readily than triphenylamine. Any quantitative conclusion of coupling rates with HMO reactivity parameters is rendered tenuous by the fact that the electrochemistry of the *meta* systems is obscure; the potentials of the initial and follow-up systems are closely spaced and the current relationships too difficult to evaluate. No unequivocal evaluation of *p*-benzidine formation was made with the *meta* compounds.

Unexpectedly, the tri-*m*-nitro derivative gave a surprisingly stable monocation radical. The epr spectrum could not be resolved well enough to assign coupling constants. The radical did decay presumably to a benzidine.

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Appendix

Syntheses of Substituted Triphenylamines. Mention should be made of the general reaction procedures employed. All of the syntheses were simply variations of the Ullmann reaction.[10] The reaction solvent was nitrobenzene, and normally 50–75 ml was used. Potassium carbonate was added to take up the HI liberated in the reaction. Copper bronze was used after it had been treated according to Vogel.[11] A pinch of iodine was added to regenerate the catalyst. The reaction was usually run for approximately 24 hr.

A tarry residue usually resulted, and this was steam distilled to remove the nitrobenzene. The organic residue was extracted into benzene and chromatographed on an alumina column.

All analyses were performed by Huffmann Laboratories, Inc., of Wheatridge, Colo. Analyses were carried out for carbon, hydrogen, and nitrogen. Any other species present were determined by difference.

A. **Substituted Triphenylamines. 1. 4-Nitro-4′,4′′-dimethoxytriphenylamine** was prepared from di-*p*-anisylamine and *p*-iodonitrobenzene. The product was chromatographed on Woelm neutral alumina with benzene. The compound oiled out repeatedly from various solvents, so it was taken to dryness, dissolved with benzene, and recrystallized from benzene–ethanol by evaporation, mp 131°.

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00; O, 18.26. Found: C, 68.81; H, 5.20; N, 7.71; O, 18.28.

2. 4,4′-Dimethoxytriphenylamine was prepared from di-*p*-anisylamine and iodobenzene. The product was chromatographed on Woelm neutral alumina with benzene and recrystallized from Skelly B, mp 107.5–108.5°.

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.8; H, 6.30; N, 4.59; O, 10.3. Found: C, 78.8; H, 6.31; N, 4.62; O, 10.2.

3. 4-Cyanotriphenylamine was prepared from *p*-aminobenzonitrile and iodobenzene. The product was chromatographed on basic alumina with benzene and recrystallized from ethanol, mp 126–127°.

Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.5; H, 5.22; N, 10.3. Found: C, 84.7; H, 5.36; N, 10.4.

4. 2-Methoxytriphenylamine was prepared from diphenylamine and *o*-iodoanisole. The product was chromatographed on basic alumina with benzene. Repeated attempts at recrystallization from various solvents were unsuccessful. The compound finally recrystallized from ethanol by evaporation, mp 74–75°.

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.9; H, 6.22; N, 5.09; O, 5.80. Found: C, 83.1; H, 6.23; N, 5.05; O, 5.63.

5. 2-Methyltriphenylamine was prepared from diphenylamine and *o*-iodotoluene. The product was chromatographed on basic alumina with benzene. Recrystallization was attempted from many solvents unsuccessfully but was finally effected from a benzene–ethanol mixture by evaporation, mp 56–58°.

Anal. Calcd for $C_{19}H_{17}N$: C, 88.0; H. 6.60; N, 5.41. Found: C, 88.2; H, 6.60; N, 5.41.

6. 4-Nitro-4′-methoxytriphenylamine was prepared from 4-nitrodiphenylamine and *p*-iodoanisole. The product was chroma-

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(10) F. Ullmann, *Ber.*, 36, 2382 (1903).

(11) A. I. Vogel, "A Text-Book of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N. Y., 1957, p 193.

tographed on Woelm neutral alumina with benzene and recrystallized from ethanol by evaporation, mp 107–108°.

Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.2; H, 5.04; N, 8.75; O, 15.0. Found: C, 71.8; H, 5.11; N, 8.30; O, 14.7.

7. 2-Chlorotriphenylamine was prepared from diphenylamine and *o*-iodochlorobenzene. The crude product was chromatographed on basic alumina. An oil was obtained repeatedly on attempted recrystallizations, so this oil was vacuum distilled, bp ~200° (~1 mm).

Anal. Calcd for $C_{18}H_{14}NCl$: C, 77.4; H, 5.07; N, 5.05; Cl, 12.6. Found: C, 78.1; H, 5.11; N, 5.22; Cl, 11.5.

8. 3-Methoxytriphenylamine was prepared from diphenylamine and *m*-iodoanisole. The product was chromatographed on basic alumina with benzene. An oil was obtained upon attempted recrystallization.

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.9; H, 6.22; N, 5.09; O, 5.80. Found: C, 83.3; H, 6.18; N, 5.32; O, 5.33.

9. Tri-*m*-anisylamine was prepared from *m*-anisidine and *m*-iodoanisole. The crude product was chromatographed on basic alumina with benzene and an oil was obtained from ethanol upon evaporation.

Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.3; H, 6.33; N, 4.18; O, 14.2. Found: C, 75.1; H, 6.17; N, 4.24; O, 14.5.

10. Tris(*m*-nitrophenyl)amine was prepared from *m*-nitroaniline and *m*-iodonitrobenzene. The tar was dissolved by refluxing with benzene for 48 hr. The crude product was chromatographed on neutral alumina with benzene. The first band to come off was a side product, 3,3′-dinitrobiphenyl. The next fraction was collected and passed through a column again, and most of the remaining biphenyl was removed. The second band was collected and the pure product was obtained by recrystallization from benzene–ethanol, mp 232–233°.

Anal. Calcd for $C_{18}H_{12}N_4O_6$: C, 56.8; H, 3.18; N, 14.7; O, 25.3. Found: C, 57.2; H, 3.41; N, 13.6; O, 25.8.

B. Substituted Benzidines. 1. N,N′-Di-*p*-tolyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodotoluene. The product was chromatographed on basic alumina with benzene and recrystallized from methanol, mp 154–156°.

Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.3; H, 6.24; N, 5.42. Found: C, 88.1; H, 6.28; N, 5.53.

2. N,N′-Di-*p*-anisyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodoanisole. The crude product was chromatographed on basic alumina with benzene and recrystallized from benzene–methanol by evaporation, mp 154–156°.

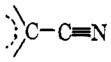
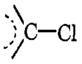
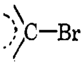
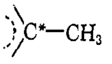
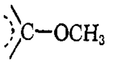
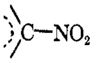
Anal. Calcd for $C_{38}H_{32}N_2O_2$: C, 83.2; H, 5.88; N, 5.11; O, 5.83. Found: C, 83.4; H, 5.98; N, 4.94; O, 5.71.

3. N,N′-Di-*p*-nitrophenyl-N,N′-diphenylbenzidine was prepared from N,N′-diphenylbenzidine and *p*-iodonitrobenzene. The product was chromatographed twice on neutral alumina with benzene and recrystallized from benzene–methanol, mp 186–189°.

Anal. Calcd for $C_{36}H_{26}N_4O_4$: C, 74.7; H, 4.53; N, 9.68; O, 11.1. Found: C, 75.5; H, 4.77; N, 9.16; O, 10.6.

Parameters for HMO Calculations. For all calculations, the following values were taken for the "central" triphenylamine nitrogen: $h_N = 1.0$, $k_{N-Cl} = 0.8$ (for all three N-phenyl carbon bonds). For a mono-*ortho*-substituted triphenylamine, the resonance integral for the pertinent N–C bond was varied from $k_{N-C} = 0.8$ *via* the usual twisting calculations. For the tri-*ortho*-substituted compounds, all three k_{N-C} values were varied simultaneously by the same amount to account for twisting.

The following heteroatom parameters were employed for the various substituents indicated.

	$k_{CC} = 0.9$, $k_{CN} = 2.0$, $h_N = 1.0$, $h_{C(cyano)} = 0.0$
	$k_{CCl} = 0.4$, $h_{Cl} = 2.0$
	$k_{CBr} - 0.3$, $h_{Br} = 1.5$
	$h_{C^*} = -0.3$ (inductive model, neglecting methyl C)
	$h_{CO} = 0.8$, $h_O = 2.0$ (methyl carbon neglected)
	$k_{CN} = 1.2$, $h_N = 2.2$, $k_{NO} = 1.67$, $h_O = 1.4$

Far-Infrared Intensity Studies of Complexes of Some Pyridine Bases with Iodine Monochloride

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Abstract: Studies are reported of the far-infrared spectra of complexes of ICl with pyridine, 3-picoline, and 2,6-lutidine. The frequencies and the intensities are given for both the I–Cl stretching vibration (~290 cm^{-1}) and the N–I stretching vibration (115–140 cm^{-1}) measured for complexes dissolved in benzene. The measurements were made with a Beckman IR-11 far-infrared spectrometer, using polyethylene cells. Experimental techniques for intensity measurements in this region of the spectrum are discussed. Attempts to obtain normal coordinates are described. Some interpretation is given of these results in terms of the theory presented by Friedrich and Person.

Studies of the changes in the vibrational spectra of the donor (D) and acceptor (A) molecules when they combine to form a complex have been a powerful aid in elucidating structural changes occurring in that process.[3] For example, earlier studies[4,5] of the I–Cl stretching vibration in complexes of ICl with different electron donors revealed a characteristic decrease of frequency and increase in intensity of that vibration as

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(3) See (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, 13, 107 (1962).

(4) W. B. Person, R. E. Humphrey, W. A. Deskin, and A. I. Popov, *J. Am. Chem. Soc.*, 80, 2049 (1958).

(5) W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, 82, 29 (1960).