

# Charge-Transfer Complexes of Aryl Derivatives of Group 14 and Group 15 Elements with Tetracyanoethylene

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**Abstract:** Spectral characteristics and association constants for dichloromethane solutions of 11 1:1 complexes of phenyl derivatives of C, Si, Ge, Sn, and Pb with TCNE are reported. Trends in values of  $\Delta\nu_{1/2}$ ,  $\lambda_{\max}$ , and  $K_{\text{eq}}$  for TCNE complexes of  $\text{PhCH}_3$ ,  $\text{Ph}_2\text{CH}_2$ ,  $\text{Ph}_3\text{CH}$ , and  $\text{Ph}_4\text{C}$  are interpreted in terms of hyperconjugative, inductive, and steric effects. Striking similarities in the spectra of TCNE complexes of  $\text{Ph}_4\text{C}$ ,  $\text{Ph}_4\text{Si}$ ,  $\text{Ph}_4\text{Ge}$ ,  $\text{Ph}_4\text{Sn}$ , and  $\text{Ph}_4\text{Pb}$  indicate that there is no appreciable  $\pi\pi \rightarrow d\pi$  bonding between the phenyl groups and central atoms and that the energies of the phenyl  $\pi$  orbitals are unaffected by the size or electronegativities of the central atoms. Spectral characteristics and association constants for dichloromethane solutions of 10 1:1 complexes of arylamines with TCNE in dichloromethane are reported. These complexes generally exhibit two absorbance bands. The low wavelength maxima,  $\lambda_1$  (385–415 nm), arise from phenyl  $a_2$  orbitals. The high wavelength maxima,  $\lambda_2$  (580–820 nm), arise from  $b_1$  orbitals, which are strongly conjugated with the unbonded electron pair of the central atom. Di- and triarylamines form stable complexes with TCNE, whereas monoarylamines react irreversibly with TCNE.  $\text{Ph}_3\text{P}$  reacts rapidly with TCNE in dichloromethane to yield a 1:2 adduct. TCNE also reacts rapidly with 2-, 3-, and 4-Tol<sub>3</sub>P but forms a 1:1 complex with  $\text{Ms}_3\text{P}$  which has  $\lambda_{\max}$  416 nm.  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$ , and  $\text{Ph}_3\text{Bi}$  form 1:1 complexes with TCNE which have two overlapping absorbance bands. The low wavelength bands,  $\lambda_1$  (385–405 nm), arise from  $a_2$  orbitals, whereas the high wavelength bands,  $\lambda_2$  (515–545 nm), arise from  $n$  orbitals energized by  $\pi\pi \rightarrow d\pi$  conjugation.

We recently reported that triphenylborane and tetracyanoethylene (TCNE) form a yellow  $\pi\pi$  complex in dichloromethane.<sup>1</sup> The color is due to a single absorbance band with a maximum at 385 nm (Figure 1) arising from a charge-transfer (CT) transition from the  $a_2$  and  $b_1$  orbitals of the phenyl ring (Figure 2) to the lowest electron-acceptor orbital (LEAO) in TCNE (Figure 3). The nature of the absorbance band and other supporting evidence led us to conclude that there was no appreciable interaction between the  $\pi$  electrons of the phenyl ring with the vacant 2p orbital of the boron atom. This finding prompted us to investigate the possible interactions of phenyl  $\pi$  electrons with vacant d orbitals and filled p orbitals of atoms of the elements of groups 14 and 15.

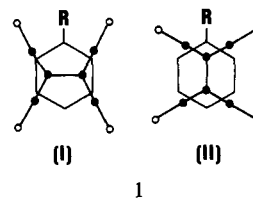
Initially we characterized TCNE complexes of phenyl derivatives of carbon and nitrogen in order to establish reference points for studies with congeners of other elements. Spectra of dichloromethane solutions of TCNE with triphenylmethane and triphenylamine in Figure 1 show evidence of electronic interaction between the phenyl groups and substituent atoms. The 815-nm band of  $\text{Ph}_3\text{N-TCNE}$  suggests particularly strong  $n \rightarrow \pi$  interaction of the nonbonded electron pair of nitrogen with the  $\pi$  electrons of the attached phenyl rings.

Previous attempts to study the nature of this interaction through characterization of arylamine-TCNE complexes have been hampered by the tendency of arylamines to undergo irreversible nitrogen- and ring-substituted tricyanovinylations with TCNE.<sup>2</sup> Nevertheless Rappoport<sup>3</sup> and Isaacs<sup>4</sup> successfully characterized complexes of TCNE with aniline and several of its derivatives.

In a typical example, Isaacs reported absorbance maxima at 400 and 643 nm in the spectrum of a dichloromethane solution of *N*-methylaniline and TCNE taken within 1 min after mixing. Combining evidence taken from optical and ESR studies of this system in dichloromethane and acetone, he concluded that the 400-nm band was due to the radical anion  $\text{TCNE}^{\cdot-}$  and that the 643-nm band arose from the  $\pi\pi$  complex  $\text{PhNHMe-TCNE}$ . While this interpretation has been confirmed specifically for  $\text{PhNHMe-TCNE}$ ,<sup>5</sup> we believe that the double bands observed

in many other arylamine-TCNE complexes can be explained by using a model proposed by Orgel<sup>6</sup> and applied to TCNE complexes by Mobley, Rieckhoff, and Voigt.<sup>7,8</sup>

According to this model, the CT transitions in the complex  $\text{PhR-TCNE}$  ( $\text{R} = \text{CH}_3, \text{OCH}_3, \text{etc.}$ ) occur between the  $a_2$  or  $b_1$  donor orbitals and the LEAO of TCNE, depending on the orientation of the molecules. The  $a_2 \rightarrow \text{TCNE}$  transition, which occurs in configuration I of 1, usually gives rise to an absorbance



band at 385 nm.<sup>9</sup> The  $b_1 \rightarrow \text{TCNE}$  transition occurs in configuration II, giving rise to a band at  $\lambda_{\max}$  greater than 385 nm when R is an electron-donating substituent. Support for this interpretation is forthcoming from our studies on TCNE complexes of aryl derivatives of nitrogen.

Bock and Alt<sup>10</sup> reported that the complexes  $\text{PhCH}_3\text{-TCNE}$  and  $\text{PhSiH}_3\text{-TCNE}$  had absorbance maxima at 406 and 385 nm, respectively. They cited these values, together with other supporting data, as evidence for  $\pi\pi \rightarrow d\pi$  interaction in which electrons are donated from the  $b_2$  orbital of the phenyl group to a vacant d orbital of the silicon atom. We have examined spectra of TCNE complexes of tetraphenyl derivatives of germanium, tin, and lead for evidence of similar interactions.

Finally we have studied the spectra of a number of phenylmethanes and arylamines for evidence of electronic and steric interactions between phenyl groups attached to a common atom.

## Experimental Section

**Reagents.** Solvents and reagent chemicals used were the purest grades available from the following chemical suppliers: Aldrich, Alfa, Fisher,

(5) Farrell, P. G.; Ngo, P. N. *J. Chem. Soc., Perkin Trans. 2* 1974, 552-556.

(6) Orgel, L. E. *J. Chem. Phys.* 1955, 23, 1352-1353.

(7) Mobley, M. J.; Rieckhoff, K. E.; Voigt, E.-M. *J. Phys. Chem.* 1978, 82, 2005-2012.

(8) Voigt, E. M. *J. Am. Chem. Soc.* 1964, 86, 3611-3617.

(9) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* 1958, 80, 2778-2782.

(10) Bock, H.; Alt, H. *J. Am. Chem. Soc.* 1970, 92, 1569-1576.

(1) Frey, J. E.; Kitchen, E. C. *J. Am. Chem. Soc.* 1983, 105, 2175-2178.  
 (2) McKusick, B. C.; Heckert, R. E.; Cairns, T. L.; Coffman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* 1958, 80, 2806-2815.  
 (3) Rappoport, Z. *J. Chem. Soc.* 1963, 4498-4500.  
 (4) Isaacs, N. S. *J. Chem. Soc. B* 1966, 1053-1058.

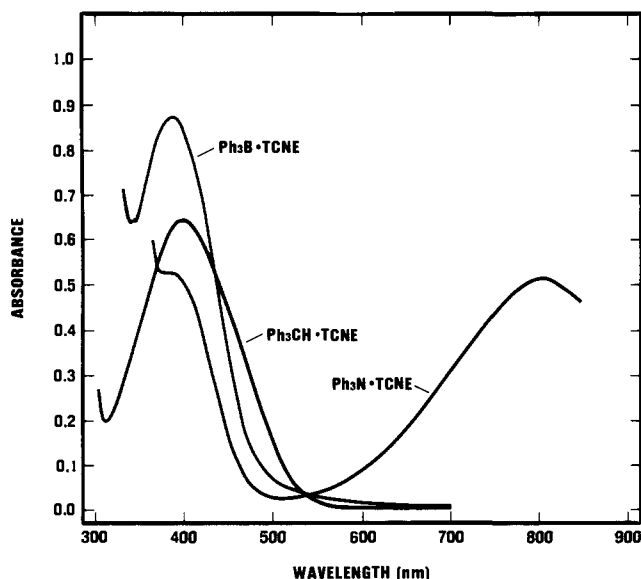


Figure 1. Absorbance curves of TCNE complexes.

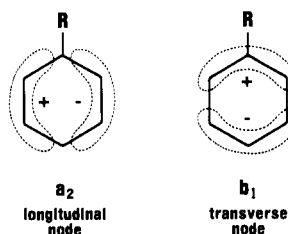


Figure 2. Highest occupied donor orbitals of the phenyl group.

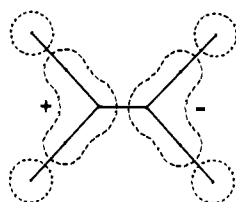


Figure 3. Lowest electron-acceptor orbital of TCNE.

Fluka, Kodak, and Petrarch Systems. All chemicals of less than "reagent grade" purity were subjected to repeated distillation, recrystallization, or vacuum sublimation until their optical spectra and melting points agreed closely with data found in the literature. TCNE from Kodak was recrystallized twice from chlorobenzene and sublimed 2 or 3 times in vacuo: mp 199–200 °C (lit.<sup>11</sup> mp 198–200 °C). Dichloromethane, Fisher Spectranalyzed, was used without further purification. Tri-4-tolylamine obtained from R. I. Walter melted sharply at 115 °C (lit.<sup>12</sup> mp 110–117 °C).

Stock solutions of all reagents in dichloromethane were prepared by transferring solids or liquids directly into tared volumetric flasks and filling to the mark with solvent. Mixtures were prepared by transferring measured amounts of stock solutions into 10-mL glass-stoppered volumetric flasks by using calibrated BDL Pipettors (precision  $\pm 0.001$  mL).

Spectra were recorded on a Beckman ACTA-CIII spectrophotometer with matched 10-mm Fisher Suprasil and 5-cm Beckman Corex quartz cells. Concentrations of stock solutions were adjusted to yield absorbance values in the range 0.2–0.8 whenever possible. Absorbance data were refined by Liptay's procedure<sup>13</sup> and fit to the Scott equation<sup>14</sup> (eq 1).  $C_X$

$$C_X C_Y / A = (1/K\epsilon) + (1/\epsilon)C_X \quad (1)$$

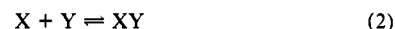
and  $C_Y$  are the molarities of reactants X and Y,  $C_X > C_Y$ , A is the

Table I. Characteristics of Charge-Transfer Complexes of TCNE with Group 14 Aryls in Dichloromethane at 21 °C

donor	$\lambda_{\max}$ , nm	$\epsilon_{\max}$	K, L/mol	$10^{-3} \Delta\nu_{1/2}$ , $\text{cm}^{-1}$
PhH <sup>a,b</sup>	385	$735 \pm 53$	$0.67 \pm 0.05$	5.7
PhCH <sub>3</sub> <sup>c</sup>	410	$1410 \pm 130$	$0.56 \pm 0.05$	6.5
PhCH <sub>2</sub> Me	415	$1520 \pm 160$	$0.41 \pm 0.04$	6.5
PhCHMe <sub>2</sub>	415	$1950 \pm 520$	$0.17 \pm 0.05$	6.7
PhCMe <sub>3</sub>	415	$630 \pm 56$	$0.46 \pm 0.04$	6.4
Ph <sub>2</sub> CH <sub>2</sub>	405	$1130 \pm 140$	$0.63 \pm 0.08$	7.3
Ph <sub>2</sub> CMe <sub>2</sub>	415	$4360 \pm 510$	$0.07 \pm 0.01$	8.0
Ph <sub>3</sub> CH	400	$316 \pm 18$	$1.34 \pm 0.08$	8.0
Ph <sub>4</sub> C	395	$254 \pm 30$	$0.85 \pm 0.10$	~8.5
Ph <sub>4</sub> Si	395	$171 \pm 17$	$2.31 \pm 0.23$	
Ph <sub>4</sub> Ge	395	$329 \pm 24$	$1.14 \pm 0.08$	
Ph <sub>4</sub> Sn	395	$237 \pm 28$	$2.36 \pm 0.28$	
Ph <sub>4</sub> Pb	395	$274 \pm 27$	$2.53 \pm 0.25$	

<sup>a</sup>Reference 9:  $\lambda$ , 384;  $\epsilon$ , 3570; K, 0.13;  $\Delta\nu_{1/2}$ , 5800. <sup>b</sup>Reference 15:  $\lambda$ , 390;  $\epsilon$ , 3000; K, 0.14. <sup>c</sup>Reference 9:  $\lambda$ , 406;  $\epsilon$ , 3330; K, 0.24;  $\Delta\nu_{1/2}$ , 6800.

absorbance of the complex XY, and K is the association constant for the complex-formation reaction (eq 2). Values of  $\epsilon$  (molar absorptivity) and



K are calculated from the slope and intercept of eq 1; their uncertainties are expressed at the 50% confidence interval. Continuous variation plots of all the complexes characterized in this study have maxima at 50 mol %, confirming the existence of 1:1 complexes in each instance.

Association constant values  $K_1$  and  $K_2$  recorded in Table II are calculated from absorbance values near the short and long wavelength bands  $\lambda_1$  and  $\lambda_2$ . Theoretically,  $K_1$  and  $K_2$  should be identical; in practice they are usually in good agreement, but in several cases they differ by a factor of 2 or 3.

**Group 14 Aryls and TCNE.** Dichloromethane solutions of the aryl derivatives listed in Table I have sharp absorbance cutoffs at 300–350 nm. When mixed with TCNE, these solutions turn yellow, the color in each instance being due to a nearly symmetrical absorbance band with  $\lambda_{\max}$  in the range 385–415 nm.<sup>9,15</sup> TCNE was used in excess in all systems involving tetraphenyl derivatives because of the limited solubility (<0.02 M) of these compounds in dichloromethane. In all other systems, the aryl derivative was used in excess.

**Arylamines and TCNE.** Dichloromethane solutions of arylamines listed in Table II have sharp absorbance cutoffs between 315–350 nm, except for tri-4-tolylamine which absorbs strongly just below 400 nm. When mixed with TCNE, these solutions turn blue or green in color. Solutions of TCNE with di- and triarylamines and with the carbazoles maintained color stability for periods of several days in contrast to TCNE-anilines which changed color within hours due to irreversible reactions between the components. Spectra of unstable systems were taken within 2 min after mixing.

**Group 15 Triphenyls and TCNE.** Dichloromethane solutions of Ph<sub>3</sub>As, Ph<sub>3</sub>Sb, and Ph<sub>3</sub>Bi have absorbance cutoffs from 315 to 350 nm. When mixed with TCNE, a red or orange color appears instantly. The color remains stable for a period of several days.

Solutions of Ph<sub>3</sub>P in either chloroform or dichloromethane have a sharp absorbance cutoff at 330 nm. When Ph<sub>3</sub>P and TCNE are mixed in chloroform, a bright red-orange color develops over a period of several seconds. Spectra of these solutions exhibit bands with maxima at 360 and 485 nm. The continuous variations curve for this system rises to a maximum at about 60 mol % TCNE and then abruptly drops to 0. When Ph<sub>3</sub>P and TCNE are mixed in dichloromethane, an intense green color forms instantly and then disappears within 1 s; a red-orange color develops thereafter. The continuous variations curves for the Ph<sub>3</sub>P-TCNE system in both chloroform and dichloromethane are highly irregular. They indicate that the reagents react rapidly and irreversibly and that the complex Ph<sub>3</sub>P-TCNE, if it forms at all, has a transitory existence.

A dichloromethane solution of Ph<sub>3</sub>PO has a sharp absorbance cutoff at 300 nm. When mixed with TCNE, it turns yellow immediately. The spectrum of the mixture has two shoulders at 390 and 415 nm which are not suitable for analysis.

An intense blue color forms instantly when dichloromethane solutions of Ph<sub>3</sub>AsO and TCNE are mixed. The blue fades rapidly to a yellow-gray color indicative of an irreversible reaction between the components.

(11) Cairns, T. L.; Carboni, R. A.; Coffman, D. D.; Engelhart, V. A.; Heckert, R. E.; Little, E. L.; McGeer, E. G.; McKusick, B. C.; Middleton, W. J.; Scribner, R. M.; Theobald, C. W.; Winberg, H. E. *J. Am. Chem. Soc.* **1958**, *80*, 2775–2778.

(12) Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999–6002.

(13) Liptay, W. Z. *Elektrochem.* **1961**, *65*, 375–383.

(14) Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787–789.

(15) Bhowmik, B. B.; Srimani, P. K. *Spectrochim. Acta, Part A* **1973**, *29A*, 935–942.

**Table II.** Characteristics of Charge-Transfer Complexes of TCNE with Group 15 Aryls in Dichloromethane at 21 °C

compound	$\lambda_1$ , nm	$\epsilon_1$	$K_1$ , L/mol	$\lambda_2$ , nm	$\epsilon_2$	$K_2$ , L/mol	$A_2/A_1^f$
PhNH <sub>2</sub> <sup>a</sup>	385			590	1790 ± 80	3.23 ± 0.15	
PhNHMe <sup>b</sup>	385			640	3320 ± 30	4.84 ± 0.04	
PhNMe <sub>2</sub> <sup>c</sup>	400	1050 ± 150	5.78 ± 0.81	675	2310 ± 180	9.18 ± 0.74	3.27
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> <sup>d</sup>				640	1630 ± 170	9.24 ± 1.01	
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	405	1540 ± 230	12.8 ± 1.9	705	3260 ± 260	21.6 ± 1.7	3.23
4-CNC <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	385 sh			630	329 ± 18	2.10 ± 0.12	4.57
Ph <sub>2</sub> NH	385	1810 ± 120	0.97 ± 0.06	755	2540 ± 230	0.96 ± 0.09	1.40
Ph <sub>2</sub> NMe	400	916 ± 47	1.83 ± 0.09	800	1570 ± 80	2.08 ± 0.11	1.94
Ph <sub>3</sub> N	390	283 ± 32	1.54 ± 0.17	815	660 ± 87	0.64 ± 0.09	1.02
(4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> N	425 sh			820	973 ± 53	0.73 ± 0.04	
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> NH <sup>e</sup>	385 sh			600	3860 ± 230	1.46 ± 0.09	
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> NPh	390	627 ± 55	1.96 ± 0.17	580	1270 ± 30	2.29 ± 0.06	2.33
				725	495 ± 25	3.46 ± 0.19	1.30
Ph <sub>3</sub> As	385	137 ± 14	3.39 ± 0.38	515	93 ± 11	2.94 ± 0.36	0.60
Ph <sub>3</sub> Sb	395	457 ± 38	1.19 ± 0.10	525	131 ± 14	2.32 ± 0.25	0.45
Ph <sub>3</sub> Bi	405	610 ± 57	1.28 ± 0.12	545	207 ± 27	1.28 ± 0.17	0.34
Ms <sub>3</sub> P	416	131 ± 10	6.87 ± 0.56				

<sup>a</sup>Reference 4:  $\lambda_2$ , 610;  $\epsilon_2$ , 1510;  $K_2$ , 5.4. <sup>b</sup>Reference 4:  $\lambda_2$ , 643;  $\epsilon_2$ , 2950;  $K_2$ , 6.9; chloroform. <sup>c</sup>Reference 3:  $\lambda_2$ , 675;  $\epsilon_2$ , 3400;  $K_2$ , 15.0; 32.5 °C; chloroform. <sup>d</sup>Reference 4:  $\lambda_2$ , 654;  $\epsilon_2$ , 2400;  $K_2$ , 7.5. <sup>e</sup>Reference 32:  $\lambda_2$ , 605;  $\epsilon_2$ , 2900;  $K_2$ , 5.12; chloroform. <sup>f</sup>Ratio of absorbances at  $\lambda_2$  and  $\lambda_1$ .

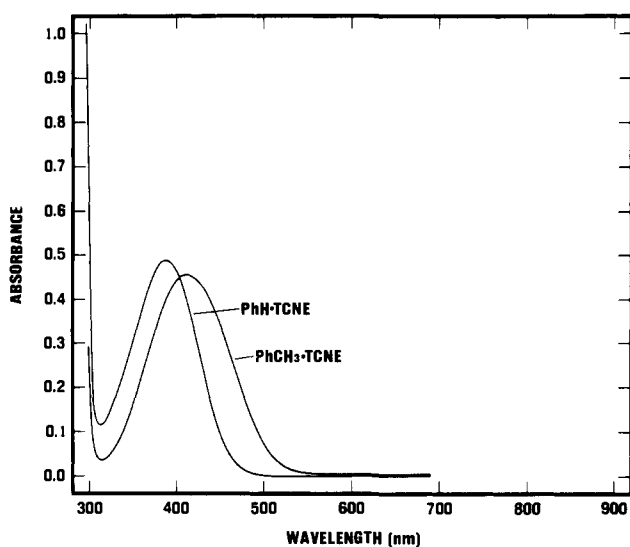


Figure 4. Absorbance curves of TCNE complexes.

When tri-2-tolylphosphine and TCNE are mixed in dichloromethane, the solution turns green initially and fades rapidly to a yellow color. A freshly mixed solution has an absorbance band at 410 nm which rapidly subsides to a shoulder. Both tri-3- and tri-4-tolylphosphine also react irreversibly with TCNE.

Trimesitylphosphine (Ms<sub>3</sub>P) forms pale yellow solutions with TCNE in dichloromethane which fade over a period of several hours. Spectra of solutions taken within 2 min after mixing indicate the presence of a 1:1 complex. The absorbance curves for these solutions exhibit a series of spikes situated at  $\lambda$  382, 390, 398, 407, 416 (max), 425, 434, 445, 454, 457 nm. The average spacing of 530 cm<sup>-1</sup> appears to be an expression of a vibrational mode in Ms<sub>3</sub>P. The spectral bands of charge-transfer complexes are usually smooth, rounded curves.

## Results and Discussion

**TCNE Complexes of Benzene and Phenylmethanes.** The spectral band of PhH-TCNE (Figure 4) has the narrowest half-width (5700 cm<sup>-1</sup>) and lowest  $\lambda_{\max}$  (385 nm) of any of the complexes considered in this study. Since the  $e_{1g}$  orbitals of benzene are degenerate, CT transitions in PhH-TCNE have the same energy and produce the same spectral band regardless of the orientations of the constituent molecules. The replacement of one hydrogen atom by a methyl group changes the symmetries of the  $e_{1g}$ (i) and  $e_{1g}$ (ii) orbitals to  $a_2$  and  $b_1$  and elevates the energy of  $b_1$  slightly above that of  $a_2$ . Consequently the spectrum of PhCH<sub>3</sub>-TCNE consists of a broadened ( $\Delta\nu_{1/2} = 6500$  cm<sup>-1</sup>), red-shifted ( $\lambda = 410$  nm) band which is a composite of two strongly overlapping bands (Figure 5) corresponding to the  $a_2 \rightarrow$  TCNE and  $b_1 \rightarrow$  TCNE transitions. This effect is also apparent in the spectra of the TCNE complexes of Ph<sub>2</sub>CH<sub>2</sub>, Ph<sub>3</sub>CH, and Ph<sub>4</sub>C (Figure 6, Table I) which

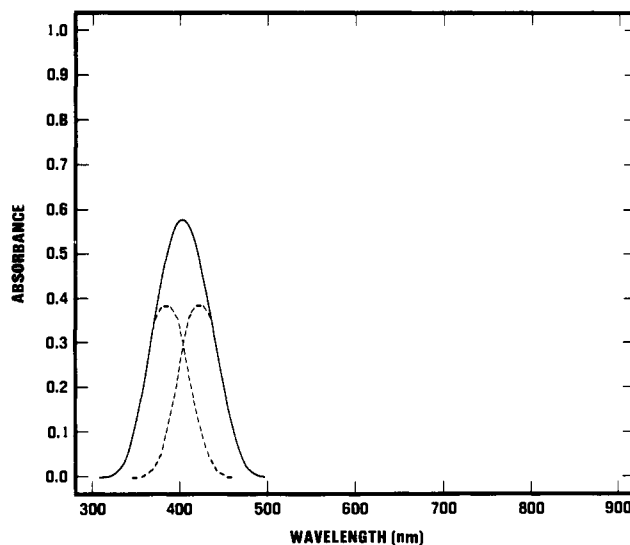


Figure 5. Deconvolution of toluene-TCNE spectra.

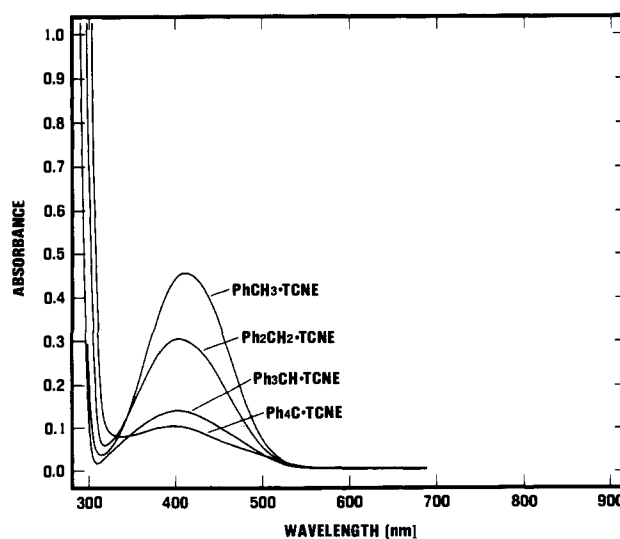


Figure 6. Absorbance curves of phenylmethane-TCNE complexes.

have  $\Delta\nu_{1/2}$  values of 7300, 8000, and  $\sim$ 8500 cm and  $\lambda_{\max}$  values of 405, 400, and 395 nm, respectively. The contrary trends in the  $\Delta\nu_{1/2}$  and  $\lambda_{\max}$  values indicate that two or more factors influence the observed spectral characteristics.

The electron-donating ability of methyl substituents is thought to arise from one or a combination of two effects: (1) hyper-

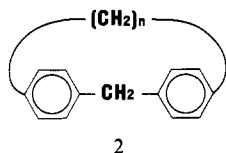
conjugation with a hydrogen atom attached to the benzylic carbon or (2) induction.

Hyperconjugation<sup>16,17</sup> provides a mechanism for conjugating C-H and C-C  $\sigma$  bonds with the  $b_1$  orbital of an adjacent phenyl ring and for releasing electrons into the ring. In the series PhCH<sub>3</sub>, Ph<sub>2</sub>CH<sub>2</sub>, Ph<sub>3</sub>CH, and Ph<sub>4</sub>C, the benzylic hydrogens are replaced successively with phenyls. This simultaneously reduces the number of hydrogens available for hyperconjugation and diffuses the electrons released thereby over a larger number of phenyls. This should lead to a progressive decline in the energies of the  $b_1$  orbitals and corresponding decreases in  $\Delta\nu_{1/2}$  and  $\lambda_{\max}$  values of TCNE complexes of members of the series.

The inductive electron-releasing ability of the benzylic carbon in a phenylmethane molecule arises from the circumstances that a ring carbon has  $sp^2$  character and the benzylic carbon attached to it has  $sp^3$  character. Consequently the ring carbon is more electronegative and draws electrons from the benzylic carbon, increasing the electron density of the phenyl ring and elevating the energy of the  $b_1$  orbital. If more than one phenyl is attached to the benzylic carbon, the electron available for release is spread over a larger number of phenyls. The electron density of the phenyl rings should diminish as the number of phenyls per molecule increases, and the energy levels of the  $b_1$  orbitals and the  $\Delta\nu_{1/2}$  and  $\lambda_{\max}$  values of the corresponding TCNE complexes should decline as well.

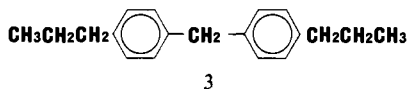
While both hyperconjugation and induction are significant factors in establishing the energy levels of the  $\pi$  electrons in the phenylmethanes, they cannot be made to account for the increase in half-bandwidths with phenyl substitution observed in TCNE complexes of the phenylmethanes. Two additional factors which may be involved are (3) transannular  $\pi$ -electron interactions and (4) steric interactions that affect the populations of isomeric complexes.

Transannular  $\pi$ -electron interactions between phenyl groups attached to a common carbon atom were studied by Cram and Bauer.<sup>18</sup> They observed that the maxima for the long wavelength bands,  $\lambda_2$ , of TCNE complexes of a series of closed-chain [1,*n*]paracyclophanes (**2**) decrease progressively from 527 nm ( $n = 7$ ) to 490 nm ( $n = 12$ ) as the separation between the phenyl groups increases. Furthermore, the TCNE complex of the related



open-chain compound, 1,1-bis(4-*n*-propylphenyl)methane (**3**), has a  $\lambda_2$  of 460 nm which is identical with that of *p*-xylene-TCNE.

These data suggest that transannular  $\pi$ -electron interactions decrease as the separation between phenyls increases and that it is negligible for open-chain compounds which have two phenyls joined to a common carbon atom. Since the  $\lambda_{\max}$  values of the



phenylmethane-TCNE complexes decrease with increasing phenyl substitution, i.e., from 410 nm for PhCH<sub>3</sub>-TCNE to 395 nm for Ph<sub>4</sub>C, we conclude that transannular  $\pi$ -electron interaction is a negligible effect even in Ph<sub>3</sub>CH and Ph<sub>4</sub>C under the conditions of our study.

On the other hand, Distefano et al.<sup>19</sup> found several unique maxima in the photoelectron spectra of Ph<sub>2</sub>CH<sub>2</sub> and Ph<sub>3</sub>CH which they attributed to intramolecular electronic interactions between

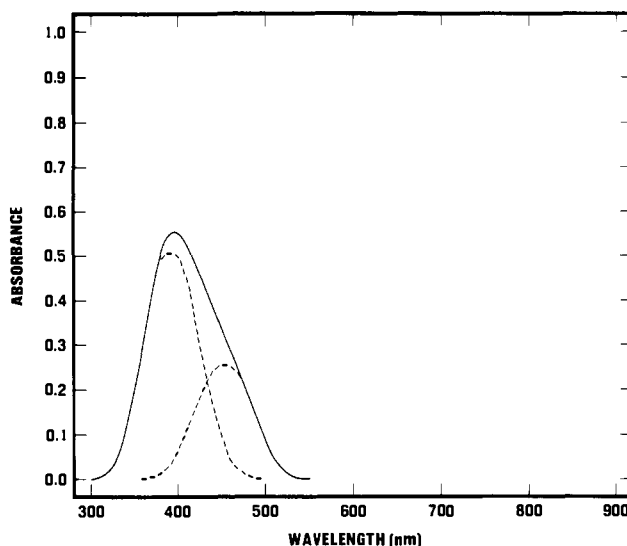


Figure 7. Resolution of bands for Ph<sub>3</sub>CH-TCNE.

phenyl rings. We believe that these observations can be explained by inductive and hyperconjugative as well as geometric effects and that they are not contrary to our own observations.

Intermolecular steric interactions were studied by Holder and Thompson<sup>20</sup> who showed that I is less sterically hindered than II for the PhR-TCNE complexes (**1**). When R is a methyl group, the populations of I and II are nearly equal; the spectrum of PhCH<sub>3</sub>-TCNE is a single band composed of two overlapping bands of nearly equal area (Figure 5). When R is a bulky group such as *tert*-butyl or phenyl, the population of I quite exceeds that of II and the spectrum is a composite of two unequal bands similar to that shown for the resolved spectrum of Ph<sub>3</sub>CH-TCNE (Figure 7). The observed band has both a lower  $\lambda_{\max}$  and absorbance and a greater half-bandwidth than it would have had if the populations of I and II had been equal.

Applying this argument to the phenylmethane-TCNE complexes, it follows that as the number of phenyls increases in the series PhCH<sub>3</sub>, Ph<sub>2</sub>CH<sub>2</sub>, Ph<sub>3</sub>CH, and Ph<sub>4</sub>C, steric interference between TCNE and the phenyl rings increases. Consequently the population ratio, II/I, and the corresponding band-area ratio decrease, and the spectral bands of each of the complexes appear both blue-shifted and broadened with respect to the preceding member in the series. This corresponds to the trends in  $\lambda_{\max}$  and  $\Delta\nu_{1/2}$  which were determined for the TCNE complexes in this series.

Foster<sup>21</sup> has reviewed several studies which show that the association constants for CT complexes of various derivatives of benzene, stilbene, and biphenyl are strongly affected by the number of potential donor sites per molecule and the degree to which they are screened by adjacent groups. In this connection it is interesting to note that the *K* values of TCNE complexes of PhCH<sub>3</sub>, Ph<sub>2</sub>CH<sub>2</sub>, Ph<sub>3</sub>CH, and Ph<sub>4</sub>C are 0.56, 0.63, 1.84, and 0.85 L/mol, respectively (Table I). This trend may be rationalized by noting that as the number of donor sites (phenyl faces) per phenylmethane molecule increases, the steric screening of these sites by adjacent phenyls increases as well. Examination of space-filling molecular models of the phenylmethanes indicates that Ph<sub>3</sub>CH has the largest number of unhindered phenyl faces; Ph<sub>3</sub>CH-TCNE has the highest *K* value as well.

In summary, we can best account for the trends observed in the  $\Delta\nu_{1/2}$ ,  $\lambda_{\max}$ , and *K* values of the phenylmethane-TCNE complexes by assuming that the energy levels of the  $b_1$  orbitals of the phenylmethane molecules are determined primarily by intramolecular C-H hyperconjugation and/or induction and that the populations of the two isomeric forms of the complexes are de-

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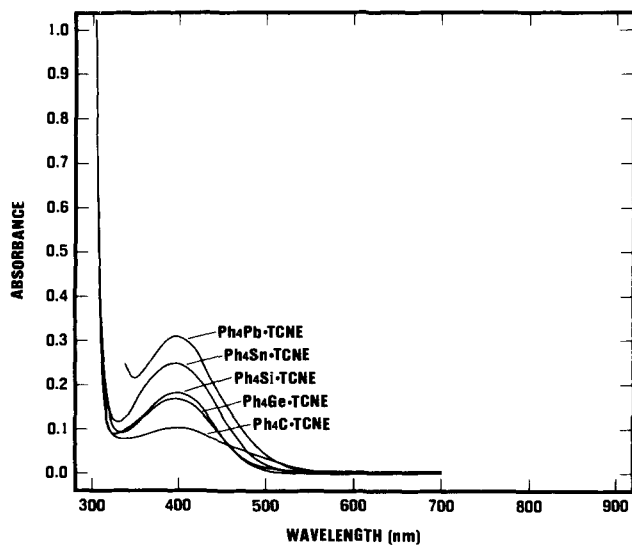


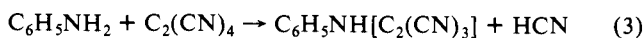
Figure 8. Absorbance curves for  $\text{Ph}_4\text{M-TCNE}$  complexes.

terminated by steric interactions between TCNE and the phenyl rings.

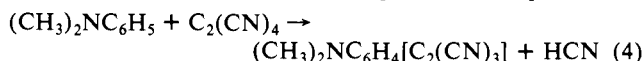
**Group 14 Tetraphenyls and TCNE.** The TCNE complexes of  $\text{Ph}_4\text{C}$ ,  $\text{Ph}_4\text{Si}$ ,  $\text{Ph}_4\text{Ge}$ ,  $\text{Ph}_4\text{Sn}$ , and  $\text{Ph}_4\text{Pb}$  have similar association constants (Table I) and identical  $\lambda_{\text{max}}$  values at 395 nm (Figure 8). Alt and Bock<sup>10</sup> cite the low  $\lambda_{\text{max}}$  of  $\text{PhSiH}_3\text{-TCNE}$  at 385 nm relative to  $\lambda_{\text{max}}$  of  $\text{PhCH}_3\text{-TCNE}$  at 406 nm as evidence for  $p\pi \rightarrow d\pi$  donation from the phenyl to vacant d orbitals of silicon. The equality in  $\lambda_{\text{max}}$  values for all  $\text{Ph}_4\text{M-TCNE}$  complexes is evidence for the absence of  $p\pi \rightarrow d\pi$  interaction as well as effects due to electronegativity and atomic size of the central atoms in  $\text{Ph}_4\text{M}$  compounds.

**TCNE Complexes of Phenylalkanes.** The TCNE complexes of the monophenylalkanes  $\text{PhCH}_3$ ,  $\text{PhCH}_2\text{Me}$ ,  $\text{PhCHMe}_2$ , and  $\text{PhCMe}_3$  (Table I) have spectral characteristics and association constants which are similar in all respects. This suggests that a benzylic hydrogen and a benzylic methyl group each exert about the same electron-releasing effect on the adjacent phenyl ring.

**Arylamines and TCNE.** Most monoarylamines react with TCNE by a complicated sequence of reactions, yielding N- or ring-substituted tricyanovinyl derivatives as the final products.<sup>11</sup> A primary arylamine such as aniline undergoes rapid N-substitution by TCNE (eq 3). A dialkylarylamine such as *N,N*-di-



methylaniline yields a ring-substituted derivative with the tricyanovinyl group preferentially attached in the para position (eq 4). These reactions have hampered previous attempts to char-



acterize arylamine-TCNE complexes and to clarify the nature of their spectra.

Some di- and triarylamines, however, form stable equilibrium systems with TCNE which are free of interfering reaction intermediates and products; these systems can be characterized with greater precision. Arylamine-TCNE systems generally exhibit two absorbance bands (Table II) which have  $\lambda_{\text{max}}$  values in the range 385–405 nm for the low band,  $\lambda_1$ , and 580–820 nm for the high band,  $\lambda_2$ . A dichloromethane solution of  $\text{Ph}_3\text{N}$  and TCNE, for example, is green and has maxima at 385 and 815 nm. Continuous variations and Scott analyses using either band confirm the presence of  $\text{Ph}_3\text{N-TCNE}$  in stable equilibrium with its constituents. The similarity of the  $\lambda_{\text{max}}$  of the low-wavelength band with that of  $\text{PhH-TCNE}$  (385 nm) suggests that this band is due to a transition from an  $a_2$ -type orbital to TCNE. The high-wavelength band is attributed to a transition of a  $b_1$ -type orbital to TCNE.

Systems containing a monoarylamine and TCNE change color appreciably within several minutes or hours. A freshly prepared dichloromethane solution of  $\text{PhNH}_2$  and TCNE is blue with

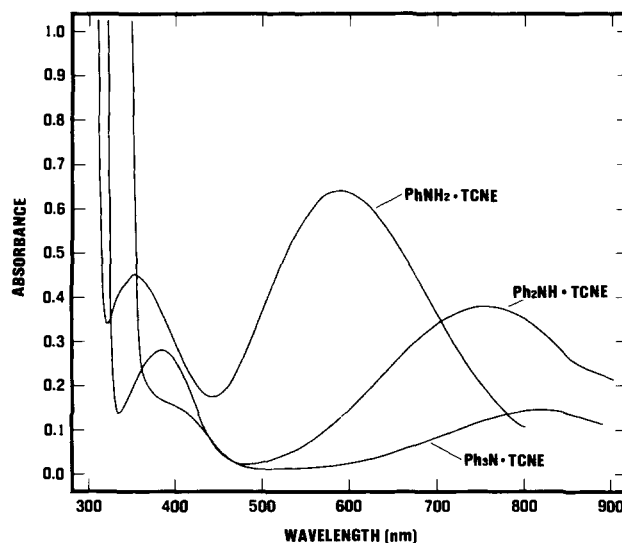


Figure 9. Absorbance curves of phenylamine-TCNE complexes.

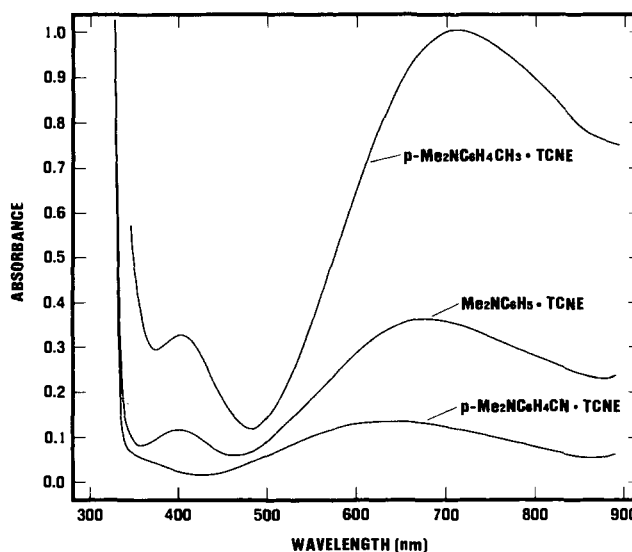


Figure 10. Absorbance curves of *N,N*-dimethylaniline-TCNE derivatives.

maxima at 385 and 590 nm (Figure 9). The color of this solution deepens rapidly as the absorbance maximum of the 385-nm band simultaneously increases in intensity and shifts to 350 nm. Continuous variations and Scott analyses of the 590-nm band using freshly mixed solutions confirms the presence of  $\text{PhNH}_2\text{-TCNE}$  in the solution. A similar analysis of the 385-nm band fails because of the rapid changes taking place in the spectra in that region. Our observations indicate that the initial absorbance band at 385 nm is due to the complex  $\text{PhNH}_2\text{-TCNE}$  and that subsequent changes in this band are due to the buildup of products of an irreversible reaction between  $\text{PhNH}_2$  and TCNE. This sequence is in general agreement with the mechanistic pathway proposed by Rappoport<sup>3</sup> and Nogami et al.<sup>22</sup> for the reaction of *N*-alkylamines and TCNE.

The preceding interpretation of the origin of the spectral bands is supported by studies of the effect of electron-releasing and -withdrawing substituents on the spectra of arylamine-TCNE complexes. We previously noted that a methyl substituent on a phenyl ring releases electrons into the ring and increases the energy of the  $b_1$  orbitals. This effect is responsible for the difference in  $\lambda_{\text{max}}$  of  $\text{PhH-TCNE}$  (385 nm) and  $\text{PhCH}_3\text{-TCNE}$  (410 nm). This same trend is observed in comparing the  $\lambda_{\text{max}}$  of  $\text{Ph}_3\text{N-TCNE}$  (385 and 815 nm) with those of  $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{N-TCNE}$  (425 and 820 nm). The effect is seen more dramatically in the  $\lambda_{\text{max}}$  shifts (Figure 10) in the TCNE complexes of 4-(dimethyl-

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Table III. Ionization Energies of Arylamines

compound	$I_D$ , eV <sup>a</sup>		$I_p$ , eV	
	$\lambda_1$	$\lambda_2$	$a_2$	$b_1$
PhNH <sub>2</sub> <sup>b</sup>	9.09	7.78	9.12	8.02
Ph <sub>2</sub> NH <sup>c</sup>	9.09	7.25	9.25	7.44, 9.04
Ph <sub>3</sub> N <sup>b</sup>	9.04	7.11	8.80	6.99
PhNHMe <sup>c</sup>	9.09	7.59	9.05	7.65
PhNMe <sub>2</sub> <sup>c</sup>	8.95	7.47	9.00	7.45
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> <sup>d</sup>	8.91	7.38	8.86	7.27
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> <sup>d</sup>		7.59	8.94	7.62
Ph <sub>2</sub> NMe <sup>e</sup>	8.95	7.14	9.25	7.33, 9.08
(C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> NH <sup>e</sup>	9.09	7.74	8.08, 9.09	7.68

<sup>a</sup>  $I_D$  calculated with eq 5, ref 31. <sup>b</sup>  $I_p$  from ref 28. <sup>c</sup>  $I_p$  from ref 29. <sup>d</sup>  $I_p$  from ref 30. <sup>e</sup>  $I_p$  from ref 27.

amino)benzotrile (385 sh, 630 nm) and *N,N*-dimethylaniline (400 and 705 nm). Here the electron-withdrawing *p*-cyano substituent produces a blue shift in both bands with respect to *N,N*-dimethylaniline, whereas the *p*-methyl substituent produces a red shift. These comparisons show that ring substituents superimpose their own effects on the energies of the  $\pi$  electrons independently of the amino group.

The long wavelength bands,  $\lambda_2$ , of the TCNE complexes of PhNH<sub>2</sub>, Ph<sub>2</sub>NH, and Ph<sub>3</sub>N (Figure 9) have values of 600, 755, and 815 nm (Table II). The magnitude of these values and their large variation suggest that these bands arise from electronic transitions involving  $b_1$ -type orbitals which are conjugated with the nonbonded electron pair of the substituent nitrogen. Dewar and Dougherty<sup>23</sup> point out that conjugation between the nitrogen and phenyl groups in arylamines increases as the arrangement of bonds around the nitrogen atom approaches planarity. In the planar conformation the nonbonded electron pair (*n*) of nitrogen has *p* character, and the plane of the  $b_1$  orbital is oriented at 90° to the axis of the *n* orbital.

Bond angles reported for the phenylamines (PhNH<sub>2</sub>,<sup>24</sup>  $\angle$ HNH = 113 ± 2°; Ph<sub>2</sub>NH,<sup>25</sup>  $\angle$ CNC = 126°; Ph<sub>3</sub>N,<sup>26</sup>  $\angle$ CNC = 116 ± 2°) indicate that the tendency toward planarity in these molecules, PhNH<sub>2</sub> < Ph<sub>2</sub>NH < Ph<sub>3</sub>N, parallels the increase in  $\lambda_2$  values 600 nm < 755 nm < 815 nm, of the phenylamine-TCNE complexes. The trend in bond angles suggests increasing steric crowding of the phenyl groups; the trend in  $\lambda_2$  values suggests a tendency toward greater *n* →  $\pi$  conjugation and higher  $b_1$  energies in this series.

The assignment of  $\lambda_1$  and  $\lambda_2$  bands of monoarylamines-TCNE complexes to  $a_2$  and  $b_1$  transitions is supported by ionization energies ( $I_p$ ) obtained from several photoelectron spectral studies<sup>27-30</sup> (Table III). These  $I_p$  values agree closely with ionization energies ( $I_D$ ) calculated for donor molecules in TCNE complexes using the Voigt-Reid<sup>31</sup> equation

$$I_D = \left( \frac{1204}{\lambda_{\max}} + 4.42 \right) / 0.83 \quad (5)$$

The assignment of  $\lambda_2$  bands of di- and triarylamines complexes is less straightforward due to the close spacing of the lower energy  $\pi$  orbitals.

***N*-Methylarylamines and TCNE.** In his studies of arylamine-TCNE complexes, Isaacs<sup>4</sup> showed that  $\lambda_{\max}$  values for the long-wavelength band,  $\lambda_2$ , of *N*-methylarylamines-TCNE complexes are higher than the  $\lambda_2$  values for the corresponding unsubstituted arylamine-TCNE complexes. Our studies confirm

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(24) Lister, D. G.; Tyler, J. K.; Hög, J. H.; Larsen, N. W. *J. Mol. Struct.* **1974**, *23*, 253-264.

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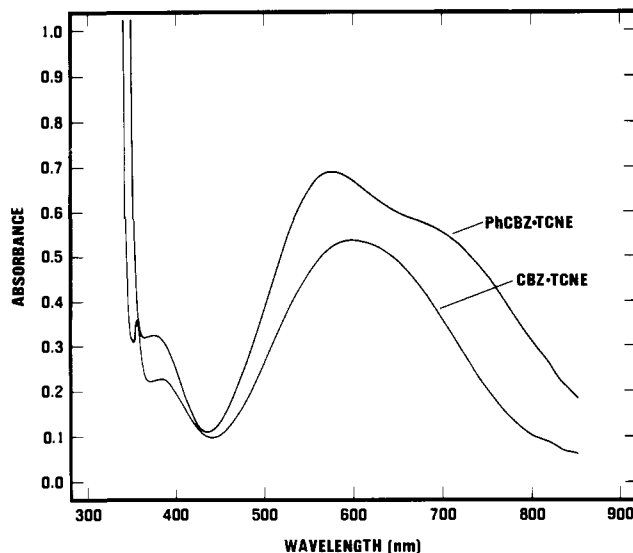


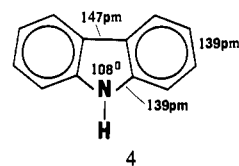
Figure 11. Absorbance curves of carbazole-TCNE complexes.

Isaacs' findings and show that the values of  $\lambda_1$  and association constants increase with *N*-methyl substitution as well. The effects on  $\lambda_1$ ,  $\lambda_2$ , and  $K_2$  are seen in the following series: Ph<sub>2</sub>NH-TCNE (385, 755, and 0.96) < Ph<sub>2</sub>NMe-TCNE (400, 800, and 2.08), and PhNH<sub>2</sub>-TCNE (385, 600, and 3.23) < PhNMe-TCNE (395, 640, and 4.84) < PhNMe<sub>2</sub>-TCNE (400, 675, and 9.18). The data indicate that the electron-releasing ability of methyl groups is transmitted through nitrogen atoms to elevate the energy of conjugated phenyl  $b_1$  orbitals and increase the donor abilities of aromatic amines toward TCNE.

The  $\lambda_2$  values observed for PhNMe and 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (Table II) are nearly identical at 640 nm. This suggests that a para-substituted methyl and a *N*-substituted methyl each exert about the same electron-releasing effect on an aniline system.

Our assignments of  $\lambda_1$  and  $\lambda_2$  to the  $a_2$  and  $b_1$  orbitals of *N*-methylarylamines-TCNE complexes are supported by PES studies (Table III) which yield  $I_p$  values in good agreement with  $I_D$  values for PhNHMe, PhNMe<sub>2</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>, and Ph<sub>2</sub>NMe.

**Carbazoles and TCNE.** Carbazole (CBZ) (4) forms a stable 1:1 complex with TCNE,<sup>32</sup> which is of interest because of its similarity to Ph<sub>2</sub>NH-TCNE (Figure 11). Both CBZ and Ph<sub>2</sub>NH



have phenyl groups mutually joined to the nitrogen; the phenyls in CBZ are cojoined at the ortho positions by a C-C bond which forces them into a coplanar conformation and provides a possible conduit for interring conjugation. The structural and orbital differences are reflected in the  $\lambda_1$  and  $\lambda_2$  values for Ph<sub>2</sub>NH-TCNE (385 and 755 nm) and CBZ-TCNE (385 and 600 nm).

Structural studies of Ph<sub>2</sub>NH<sup>25</sup> and CBZ<sup>33</sup> show that (1) the N-H bonds in neither compound are coplanar with the phenyl rings, (2) the C-N bond lengths in Ph<sub>2</sub>NH (140 pm) and CBZ (139.4 pm) are shorter than the C-N single-bond length (147 pm), and (3) the C-C bond length between the cojoined phenyls in CBZ (147.9) is about midway between the C-C single-bond length (154 pm) and the intraring C-C bond length in benzene (139 pm). These data, together with evidence from UV spectra and nitration reactions of CBZ,<sup>34</sup> indicate that interring  $\pi$ - $\pi$  conjugation is of lesser significance than *n*- $\pi$  conjugation in CBZ.

Haink, Adams, and Huber<sup>27</sup> correlated the first three PES bands of CBZ with the orbitals  $\pi_7$ ,  $\pi_6$ , and  $\pi_5$  (Figure 12). The

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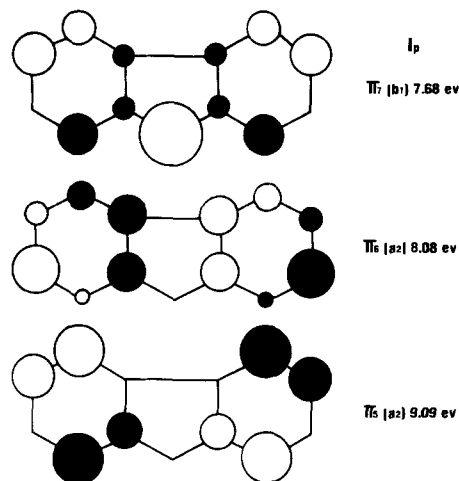
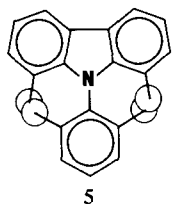


Figure 12. Highest occupied orbitals of carbazole.

$I_p$  values of these bands, 7.68, 8.08, and 9.09 eV, correspond to  $\lambda$  values 616, 527, and 385 nm as calculated by eq 5. Since the calculated  $\lambda$  values, 616 and 527 nm, bracket  $\lambda_2$ , 600 nm, for CBZ-TCNE, and since this band is quite broad ( $\Delta\nu_{1/2} = 6250 \text{ cm}^{-1}$ ), it is reasonable to assume that the  $\lambda_2$  band is a composite of two overlapping bands with  $\lambda_{\text{max}}$  at about 650 and 550 nm, arising from  $\pi_7$  and  $\pi_6$  transitions, respectively. The  $\lambda_1$  band at 385 nm can be assigned unequivocally to a  $\pi_5$  transition.

This interpretation is supported by data obtained from the spectrum of PhCBZ-TCNE (5) (Figure 11) which exhibits a shoulder at 390 nm and two distinctly overlapping bands with  $\lambda_{\text{max}}$  at about 580 and 725 nm. Consideration of a space-filling model



of PhCBZ shows that steric crowding of the phenyls tends to force the three C-N bonds toward a coplanar conformation. The cojoined phenyls are then in nearly optimal alignment for  $n \rightarrow \pi$  conjugation. The free phenyl, however, is prevented from becoming coplanar with the rest of the molecule because of steric interference between the four ortho hydrogens shown in 5. Nevertheless the interplanar angles of the free and cojoined phenyls is small enough to allow some conjugation between the free phenyl and the  $n$  electrons.

Since  $\pi_7$  (Figure 12) has an anti node at the point of attachment of the free phenyl, this orbital will be somewhat perturbed, and its energy will be correspondingly increased. The orbitals  $\pi_5$  and  $\pi_6$  have nodes at the nitrogen atom and will be perturbed only slightly by interaction with the free phenyl. According to our estimates, the three highest energy orbitals,  $\pi_7$ ,  $\pi_6$ , and  $\pi_5$ , are shifted from 650 to 725 nm, from 550 to 580 nm, and from 385 to 390 nm in going from CBZ to PhCBZ. The expected pattern of wavelength shifts observed for these bands indicates that the assignments are probably correct.

We conclude that  $\lambda_1$  in CBZ-TCNE and PhCBZ-TCNE arises from a  $\pi_5$  transition and that high wavelength bands in these complexes are composite bands arising from  $\pi_6$  and  $\pi_7$  transitions.

**Group 15 Triaryls and TCNE.** Preer, Tsay, and Gray<sup>35</sup> reported that solutions of  $\text{Ph}_3\text{P}$  and TCNE in chloroform have absorbance bands with  $\lambda_{\text{max}}$  374 and 502 nm. They assumed that these bands were due to the complex  $\text{Ph}_3\text{P}\cdot\text{TCNE}$ . However, our continuous variations plots of solutions of these reagents in both chloroform and dichloromethane failed to confirm the presence of any complex between them. Reddy and Weis<sup>36</sup> reported that  $\text{Ph}_3\text{P}$  and TCNE reacted exothermically in acetonitrile to produce the colorless 1:2

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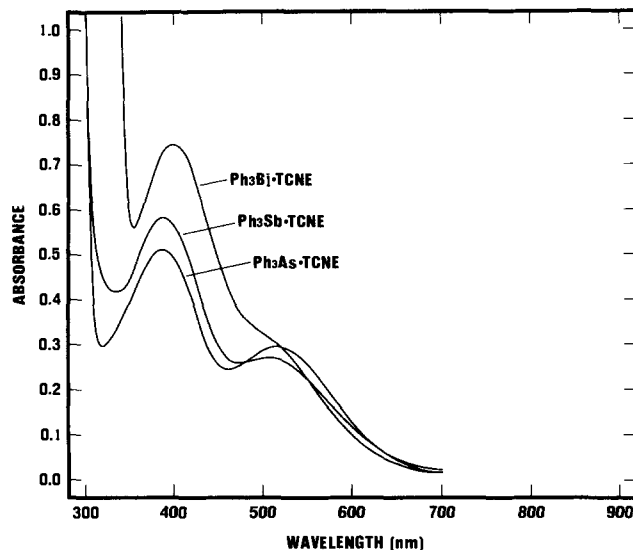
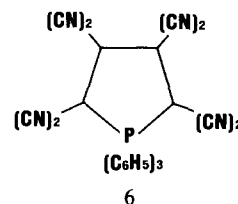


Figure 13. Absorbance curves of  $\text{Ph}_3\text{M}\cdot\text{TCNE}$  complexes.

adduct, octacyano-*P,P,P*-triphenylphosphacyclopentane (6).

Spectra of dichloromethane solutions of TCNE with  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$ , and  $\text{Ph}_3\text{Bi}$  feature two strongly overlapping bands with  $\lambda_{\text{max}}$  values in the ranges 385-405 and 515-545 nm (Figure 13).



Continuous variations and Scott analyses of the spectra of these solutions indicate the presence of weak complexes of the type  $\text{Ph}_3\text{M}\cdot\text{TCNE}$  ( $\text{M} = \text{As}, \text{Sb}, \text{and Bi}$ ) in equilibrium with their components. The spectrum of a dichloromethane solution of  $\text{Ph}_3\text{PO}$  and TCNE, in contrast, showed a single poorly defined absorbance band at 300-400 nm and no absorbance at all above 400 nm.

Evidence that the spectral bands of the  $\text{Ph}_3\text{M}\cdot\text{TCNE}$  complexes may arise from conjugated  $\pi$  orbitals is provided by the studies of Jaffé on the ultraviolet spectra of phenyl derivatives of group 15 elements.<sup>37</sup> He showed that extensive  $n \rightarrow \pi$  conjugation occurs when atoms with nonbonded electron pairs such as S, N, P, As, Sb, and Bi are attached to phenyl groups and that  $n \rightarrow \pi$  conjugation with N is stronger than conjugation with P, As, Sb, and Bi. Related compounds without unshared electron pairs, such as  $\text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ , and  $\text{Ph}_3\text{SbCl}_2$  exhibit the well-defined vibrational structure characteristic of unperturbed phenyl rings, while bands associated with conjugative interaction are absent. While these observations provide strong evidence for the involvement of conjugated nonbonded electrons in the formation of group 15-TCNE complexes, they do not explain some striking differences between  $\text{Ph}_3\text{N}\cdot\text{TCNE}$  and  $\text{Ph}_3\text{M}\cdot\text{TCNE}$  complexes ( $\text{M} = \text{As}, \text{Sb}, \text{and Bi}$ ) nor do they explain the anomalous reactivity of  $\text{Ph}_3\text{P}$  with TCNE.

A close examination of the spectral characteristics of phenylamine-TCNE and  $\text{Ph}_3\text{M}\cdot\text{TCNE}$  complexes (Table II) reveals that  $\lambda_1$  and  $\epsilon_1$  values are fairly similar. However,  $\lambda_2$ ,  $\epsilon_2$ , and  $A_2/A_1$  values for these two groups of compounds differ in three respects: (1)  $\lambda_2$  values for phenylamine-TCNE's are larger (590-815 nm) than those for  $\text{Ph}_3\text{M}\cdot\text{TCNE}$ 's (515-545 nm); (2)  $\epsilon_2$  values for phenylamine-TCNE's are larger (660-2540) than those for  $\text{Ph}_3\text{M}\cdot\text{TCNE}$ 's (100-200); and (3)  $A_2/A_1$  values for phenyl-

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**Table IV.** Ionization Energies of Triphenyl Derivatives of N, P, As, Sb, and Bi

compound	$I_D$ , eV <sup>a</sup>		$I_P$ , eV		
	$\lambda_1$	$\lambda_2$	$b_1$	$a_2$	$n$
Ph <sub>3</sub> N <sup>b</sup>	9.04	7.11	6.99	8.80	10.27
Ph <sub>3</sub> P <sup>b</sup>			10.90	9.25	7.88
Ph <sub>3</sub> As <sup>b</sup>	9.09	8.14	10.40	8.90	7.95
Ph <sub>3</sub> Sb <sup>b</sup>	9.00	8.09	10.09	9.14	8.18
Ph <sub>3</sub> Bi	8.91	7.99			

<sup>a</sup>  $I_D$  calculated with eq 5, ref 31. <sup>b</sup>  $I_P$  from ref 28.

amine-TCNE's are greater than unity (1.02-1.40) while  $A_2/A_1$  values for Ph<sub>3</sub>M-TCNE's are less than unity (0.34-0.60). These comparisons indicate that there is a fundamental difference in the mode of interaction of TCNE with the HOMO's of the phenylamines and those of Ph<sub>3</sub>As, Ph<sub>3</sub>Sb, and Ph<sub>3</sub>Bi.

On the basis of PES data and CNDO/2 calculations, Debies and Rabalais<sup>28</sup> concluded that the energies of the highest occupied orbitals in phenylamines decreased in the order  $b_1 > a_2 > n$ , whereas the energies of the highest occupied orbitals in Ph<sub>3</sub>M compounds decreased in the order  $n > a_2 > b_1$ . They attributed this reversal of  $n$  and  $b_1$  orbital energies primarily to shifts of electron density to the central atom by  $p\pi \rightarrow d\pi$  interactions in the Ph<sub>3</sub>M compounds, which result in an increase of the electron density on the central atoms in the order  $N < Sb < As < P$ .

The correlation of  $I_P$  values of Ph<sub>3</sub>N, Ph<sub>3</sub>As, and Ph<sub>3</sub>Sb with  $I_D$  values of the corresponding TCNE complexes (Table IV) suggests that  $\lambda_1$  bands in Ph<sub>3</sub>N-TCNE and Ph<sub>3</sub>M-TCNE complexes arise from an  $a_2$  transition, whereas the  $\lambda_2$  bands arise from delocalized  $b_1$  orbitals in phenylamine-TCNE's and from localized  $n$  orbitals in Ph<sub>3</sub>M-TCNE's. This difference in the nature of the HOMO of the phenylamines ( $b_1$ ) and Ph<sub>3</sub>M compounds ( $n$ ) apparently gives rise to the differences in the  $\lambda_2$  bands for the TCNE complexes of these two classes of compounds. The observed trends in electron density on the central atoms of these compounds are consistent with the reactivity of TCNE with Ph<sub>3</sub>P and the tri-*ortho*-phosphines relative to triaryl derivatives of N, As, Sb, and Bi if it is assumed that the reaction depends upon the interaction

of the highly electrophilic TCNE with a negatively charged central atom.

The structure of Ms<sub>3</sub>P and its behavior toward TCNE are of interest in this connection. A structural study<sup>38</sup> of Ms<sub>3</sub>P indicates a mean bond angle  $\angle CPC$  of 109.7° compared to 103° for Ph<sub>3</sub>P. The extraordinary flattening of Ms<sub>3</sub>P is attributed to strong steric repulsions between *o*-methyl groups on adjacent rings which incidentally almost completely shield the phosphorus atom. The very low rate of reaction of Ms<sub>3</sub>P and TCNE is probably due to the inability of TCNE to interact effectively with the  $n$  electrons of the hindered phosphorus atom. Consequently, the formation of Ms<sub>3</sub>P-TCNE must involve a charge-transfer interaction between TCNE and either or both of the  $a_2$  and  $b_1$  orbitals of the mesityl groups. The spectrum of Ms<sub>3</sub>P-TCNE consists of a single band with  $\lambda_{max}$  416 nm. The related complexes MsH-TCNE<sup>9</sup> and Ms<sub>3</sub>B-TCNE also have single bands with  $\lambda_{max}$  461 and 475 nm, respectively. The lower  $\lambda_{max}$  value of Ms<sub>3</sub>P-TCNE is expected because of electron withdrawal from the rings through  $p\pi \rightarrow d\pi$  interactions.

In summary, the chemical behavior of TCNE with aryl derivatives of group 15 elements and the characteristics of their complexes indicate that (1) the lowest energy CT transitions between TCNE and arylamines involve the  $b_1$  and  $a_2$  orbitals on the aromatic ring which are energized by  $n \rightarrow \pi$  conjugation, (2) the lowest energy CT transitions between TCNE and aryl derivatives of P, As, Sb, and Bi generally involve the  $n$  electrons on the central atom which are energized by  $p\pi \rightarrow d\pi$  conjugation, and (3) the rate of irreversible reactions of TCNE with group 15 aryls is influenced by the magnitude of the negative charge on the central atom and its steric accessibility.

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## Chemical Reactions on Clusters. 4. Gas-Phase Unimolecular Decomposition of the Acetone and Acetone-*d*<sub>6</sub> Ions in Association with Argon and Carbon Dioxide Clusters

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**Abstract:** Ion clusters of the type  $Ar_n \cdot (CD_3)_2CO^+$ ,  $Ar_n \cdot (CH_3)_2CO^+$ , and  $(CO_2)_n \cdot (CH_3)_2CO^+$  for  $n$  up to 35 have been formed by electron impact following the adiabatic expansion of an inert gas/acetone mixture. In each case the acetone ion is observed to undergo unimolecular decomposition to give either  $X_n \cdot CD_3CO^+$  or  $X_n \cdot CH_3CO^+$ . Other product ions, such as  $CD_3^+$  and  $CH_3^+$ , which are present in the mass spectrum of the isolated ion, do not appear when acetone is clustered with either argon or carbon dioxide. Overall the product ion intensity on argon clusters is higher than that on carbon dioxide clusters. To account for these observations, a simple model is proposed in which it is assumed that unimolecular decomposition of the molecular ion and vibrational predissociation of the inert gas are in competition. Calculated results from the model suggest that the time scale for vibrational predissociation lies in the range  $10^{-12}$ - $10^{-10}$  s. Reaction products from unimolecular processes which proceed faster than  $10^{-12}$  s are observed, whereas products from those reactions which are calculated to take place on a time scale  $>10^{-10}$  s are not. The experimental results indicate that the ions  $Ar_{11} \cdot CD_3CO^+$  and  $Ar_{11} \cdot CH_3CO^+$  are particularly stable, and it is suggested that this stability is due to the formation of a "magic" number atom configuration.

A number of recent experiments have exploited the fragile nature of van der Waals (vdW) molecules in order to gain some understanding of the interactions responsible for their formation and stability.<sup>1</sup> Thus, the energy of a single infrared photon is

often sufficient to bring about the "unimolecular decomposition" of a wide range of vdW molecules.<sup>2-7</sup> The mechanism for this

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