Charge-Transfer Complexes of Tetracyanoethylene with Cycloalkanes, Alkenes, and Alkynes and Some of Their Aryl Derivatives

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Spectral characteristics (λ_{max}, $\Delta\nu_{1/2}$, ϵ) and association constants (K) of charge-transfer (CT) complexes of tetracyanoethylene (TCNE) with 89 hydrocarbon donors (D) including cycloalkanes, alkenes, alkynes, benzene, benzene-d_6, alkylbenzenes, styrenes, biphenyls, polyphenylalkenes and phenylalkynes in CH_2Cl_2 are presented. New data and reevaluation of older published data indicate that many donor/TCNE systems contain significant concentrations of the D_2(TCNE) in addition to the predominant D(TCNE) species. The donor orbitals from which CT transitions originate are determined by the correlation of λ_{max} and $\Delta\nu_{1/2}$ values of CT bands of the complexes with the ionization bands in the photoelectron spectra of the donor molecules. Positive relationships between both CT energies and thermodynamic stabilities of complexes with respect to the number and geometry of substituent alkyls are established for alkene–, alkyne–, and alkylbenzene–TCNE complexes. The K values of functionally similar complexes are related to the bulk and location of substituent alkyl groups which sterically affect the interaction of the donor molecule and TCNE. Stabilities and CT energies of complexes are correlated with intramolecular conjugative and inductive effects between functional groups, as well as geometric and structural factors that control the angular orientation of the groups to each other.

Introduction

Merrifield and Phillips[1] first reported the formation of charge-transfer (CT) complexes of tetracyanoethylene (TCNE) with cyclohexene and numerous aromatic hydrocarbons in dichloromethane (DCM). Voigt[2] and Haselbach and Rossi[3] determined that these complexes arise from a $\pi \rightarrow \pi^*$ electron transfer between the HOMO of the hydrocarbon donor (D) and the LUMO of TCNE and that the ν_{max} values of the absorbance bands of a complex depend upon the energy required to effect the electron transfer:

$$\mathrm{D} + \mathrm{TCNE} + h\nu_{CT} \Leftrightarrow \mathrm{D}^+\text{–}\mathrm{TCNE}^-$$

Although CT complexes of TCNE have been studied intensively over three decades, the complexes of several major classes of hydrocarbons including alkylbenzenes, methyl- and phenylcyclopropanes, methyl- and phenylalkynes, methylstyrenes, conjugated polyenes, and polynuclear aromatics have not been systematically characterized or have not been studied at all. Furthermore there are numerous instances of disagreement between values of association constants (K) and molar absorbances (ϵ) for the same complexes reported by different authors. For example, K values of 0.20,[1] 0.26,[4] and 0.56[5] have been reported for toluene–TCNE in DCM at 20–25 °C. To resolve some of these discrepancies, we have reexamined the literature on the TCNE complexes of methylbenzenes and of cycloalkanes, alkenes, and alkynes and their aryl derivatives and reevaluated the K and ϵ values of some of them. In this investigation, which is a continuation of work reported on TCNE complexes of aryl derivatives of elements of groups 13,[6] and 14,[5] and 15,[5] we determined characteristics of 63 new hydrocarbon/TCNE systems in DCM.

Several generalizations relating the characteristics of spectral bands and the values of association constants of donor–TCNE complexes to molecular geometry and to steric, conjugative, and inductive interactions between functional and substituent groups within the donor molecule have emerged from the systematic study of several classes of donors. Material drawn from the literature of photoelectron spectroscopy (PES) is used to relate various features of the spectral bands of donor–TCNE complexes with corresponding features of the PE ionization bands and orbitals of the donor molecules.

Ionization energies (IE) obtained by PES are correlated with specific CT bands of the complexes by means of eq 1, where $h\nu_{CT}$ is the energy of the CT band at maximum

$$h\nu_{CT}\ (\mathrm{eV}) = 0.81 I_D - 4.28 \qquad (1)$$

absorbance, I_D is the vertical IE (electronvolts) of the corresponding orbital of the donor molecule taken from PE spectra, and 0.81 and 4.28 are empirical parameters derived from data for 265 donor molecules and related donor–TCNE systems.[7] The correlation coefficient and standard deviation of eq 1 are 0.972 and 0.13 eV. The reliability of the equation is ±5% relative. For the purposes of this discussion eq 1 is used in the alternate form

$$\lambda_{max}\ (\mathrm{nm}) = 1240\ (\mathrm{eV\ nm})/(0.81 I_D - 4.28) \qquad (1')$$

where λ_{max} is the wavelength of maximum absorbance of the CT band and 1240 is a conversion factor.

Experimental Section

Reagents. Solvents and reagent chemicals are the purest grades available from the following chemical suppliers: Aldrich, Alfa, Fisher, Fluka, Frinton, Kodak, Lancaster, and Pfalz & Bauer. Reagents of less than 98% purity were subjected to repeated distillation, recrystallization, or vacuum sublimation until their optical spectra and physical constants agreed closely with data found in the literature, except where noted. Exact purities were determined by capillary column chromatography using a Hewlett-Packard HP5980A chromatograph. TCNE was recrystallized twice from chlorobenzene and sublimed two or three times in vacuo: mp 199–200 °C. Spectrograde dichloromethane was used without further purification.

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Stock solutions of all reagents in DCM were prepared by transferring solids or liquids directly into tared volumetric flasks and filling to the mark with solvent. Most weighings were made on a Sartorius R160P semimicrobalance to the nearest 0.01 mg. Mixtures were prepared by transferring measured amounts of stock solutions with calibrated BDL pipetters (precision ± 0.001 mL). All weight and volume measurements were accurate to at least ±1% relative.

Spectral Analysis. Spectra were recorded on a Beckman ACTA-CIII spectrophotometer with matched 10-, 25-, and 50-mm quartz cells at 21 °C. Concentrations of stock solutions were adjusted to yield absorbance values in the range 0.1–0.8. Absorbance values, accurate to ±0.001 absorbance unit, were refined by using Liptay's procedure[8] and fit to the Scott equation:[9]

$$C_XC_Y/A = 1/K\epsilon + (1/\epsilon)C_X \qquad (2)$$

Here C_X and C_Y are the analytical molarities of reactants X and Y, and $C_X > 10C_Y$; A is the absorbance of the complex XY, ϵ is the molar absorbance of XY, and K is the apparent association constant of XY in L/mol. Values of ϵ and K are calculated from the slope $(1/\epsilon)$ and intercept $(1/K\epsilon)$ of eq 2.

In cases where the Scott line is curved because of a possibly significant concentration of the termolecular species X_2Y, the Foster–Matheson equation,[10] eq 3, is used. Here $n = C_X/C_Y \sim 1$ and b is the cell path length; ϵ and K are calculated from the intercept and slope.

$$bC_X/A = [(n+1)/n]/\epsilon + [1/nK\epsilon]/C_X \qquad (3)$$

Continuous-variations plots of all complexes characterized in this study yield symmetrical curves with maxima at 50 mol %, indicating that 1:1 complexes are dominant in solutions where $C_X < 10C_Y$. All uncertainty values are given at the 50% confidence level, and λ_{max} values are rounded to the nearest 5 nm.

Association Constants. Deranleau[11] demonstrated on theoretical grounds that 75% of the saturation fraction curve is required to show unequivocal correspondence between the equation for the model of the system and the equation fitting the data and that the most reliable values of ϵ and K are obtained when the saturation fraction, $s = [XY]/C_Y$, lies between 0.2 and 0.8. Since most of the complexes studied in this investigation have $K < 2$, it was usually necessary to use extremely large C_X/C_Y ratios ($100 < C_X/C_Y < 1200$) to achieve saturation fraction values greater than 0.2. In some instances it was impossible to achieve sufficiently high concentration ratios because of the poor solubility of the donor and/or the low absorbance limitations of the complex.

In cases where there was disagreement between ϵ and K values reported in the literature, we repeated the determinations at various C_X/C_Y ratios to ascertain whether the differences were due to methodology, to interpretation of the data, or to variations of ϵ and K with respect to C_X/C_Y. Oftentimes systems that yield apparently straight Scott lines at relatively low C_X/C_Y ratios yield distinctly curved lines at higher ratios indicating the probable presence of complexes such as X_2Y in addition to XY. Whenever possible, determinations were carried out with TCNE in excess, although the low solubility of TCNE in DCM (about 0.09 M) severely limited the applicability of this approach. It should be noted that straight Scott lines were almost always obtained with a 10–20-fold excess of TCNE, indicating the absence of donor-(TCNE)$_2$, DT$_2$, complexes in this concentration ratio range. Since curvature in Scott lines is almost always attributable to the presence of D_2T species and since there is as yet no evidence for DT_2 species, we assume that ϵ and K values obtained from the analysis of systems where $C_D/C_T < 1/20$ are reliable measures of the characteristics of the 1:1 complex, DT.

In the study of systems in which TCNE is a solute and DCM is the solvent, an added complication arises in the calculation of K because TCNE and DCM form a complex with an association constant, K_s (s = solvent), of 0.29 L/mol as calculated by Ewall and Sonnessa.[12] These authors derived eq 4, relating the apparent

$$K_{XY} = K(1 + C_sK_s) \qquad (4)$$

association constant K (the value obtained by Scott analysis) with K_{XY} (the true association constant for XY). Here C_s is the molar concentration of the solvent and $1 + C_sK_s$ is the solvent complexation factor. In dilute solutions of DMC ($C_X < 0.1$) eq 4 takes the form of eq 5. Only in solutions with donor concentrations

$$K_{XY} = K(1 + 15.6 \times 0.29) = 5.5K \qquad (5)$$

in the 1–2 M range does the solvent complexation factor drop below 5.0. Since the solute concentrations used in this study rarely exceed 1 M, we assume that K is proportional to K_{XY} and report only K values, as is customary.

Further complications arise in concentrated solutions due to changes in solvent competition for TCNE that may yield Scott lines with negative slopes. In studies of TCNE complexes with methylcyclopropanes and alkenes, for example, where Scott analysis does yield negative slopes, we assume that K is less than 0.1 and that the spectra are due to contact–CT (CCT) interactions.

Definitive or preferred values of the parameters ϵ and K for the donor/TCNE systems presented herein are selected by using the following criteria:

(1) If the Scott lines for a specific system exhibit appreciable curvature, no values of ϵ and K are reported.

(2) If the Scott lines for a specific system are straight or exhibit marginal or doubtful curvature, the parameter values are reported over several different C_D/C_T ranges if possible. (a) When the values for the various systems are in good agreement, indicating absence of D_2T species, the results from the system having the widest saturation range are designated as definitive or preferred values. (b) If the values of the parameters change progressively with C_D/C_T ratios, the result from the system having the lowest ratio is considered to be closest to the definitive value since this is the system with the smallest relative amount of D_2T species. (c) Results from systems where $C_D/C_T < 1$ are normally designated as definitive.

Results and Discussion

The 89 complexes characterized in this study are divided into nine categories according to the functional group and structural type of the donor molecule as follows: 1, cycloalkanes; 2, alkenes; 3, alkynes; 4, benzene and deuteriobenzene; 5, alkyl- and alkenylbenzenes; 6, alkyldibenzenes and biphenyls; 7, styrenes; 8, polyphenylalkanes; 9, phenylalkynes. Donors are coded for reference in the text according to the alphanumeric character shown in column 1, Table I.

Wavelength maxima for CT bands are shown in columns 3–5. When only one band appears in a spectrum, its wavelength maximum is reported as λ_{max} in column 3. If the band appears as a shoulder on the solute cutoff, the wavelength at one-half band height is given with an sh suffix. If two distinct bands appear in the spectrum, the wavelength maxima are reported as λ_1 and λ_2 in columns 4 and 5. If the main band is deconvoluted into two overlapping bands, the values of λ_1 and λ_2 are shown in italics. The ratios of absorbances at λ_2 and λ_1, A_2/A_1, are given in column 6, and the band width at half-height, $\Delta\nu_{1/2}$, is given in column 7.

Molar absorbance values, ϵ, are given at λ_{max} or for the band with the greater absorbance in column 8. The apparent association constants, K (L/mol), for the complexes are reported in col 9. The product ϵK is a measure of the "effective absorbance" of a complex because the larger the value of ϵ and/or K, the greater the net absorbance of the complex for a given level of reagent concentrations. The ϵK values, given in column 10, are of interest because their magnitudes are characteristic of some classes of complexes; in certain cases, trends in ϵK values follow progressive

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Table I. Complexes of TCNE with Hydrocarbons in Dichloromethane at 21 °C

code	donor molecule	λ_{max}, nm	λ_1, nm	λ_2, nm	A_2/A_1	$\Delta\nu_{1/2}$, cm^{-1}	ϵ_{max}, L/(mol cm)	K, L/mol	ϵK	C_D/C_T	% satn
1A	1,1-dimethylcyclopropane	350 sh					neg			19	
1B	1,1,2-trimethylcyclopropane	385 sh					730 ± 160	0.04 ± 0.01	30	20	2–5
1C	1,1,2,2-tetramethylcyclopropane	425 sh					300 ± 42	0.04 ± 0.01	12	20	1–3
1D	adamantane	365 sh					171 ± 6	0.61 ± 0.02	100	10	8–18
	adamantane[a]	355									
1E	1,3-dimethyladamantane	365 sh					117 ± 20	0.51 ± 0.09	60	16	5–10
2A	1-hexene	355					1830 ± 510	0.03 ± 0.01	50	76	2–5
2B	*trans*-2-hexene	410				7200	cur			16	
2C	*cis*-2-hexene	415				6800	1480 ± 400	0.04 ± 0.01	60	15	1–3
2D	cyclohexene	415				6900	cur			20	
	cyclohexene[b]	422					4760	<0.01	<50		
	cyclohexene[c]	408					2000	0.03 ± 0.01	60		
	cyclohexene[d]	417									
2E	2-methyl-2-pentene	465				6500	neg			20	
2F	2,3-dimethyl-2-butene	535				6100	3030 ± 660	0.05 ± 0.01	150	20	1–3
2G	1,5-hexadiene	345					neg			20	
2H	2,5-dimethyl-1,5-hexadiene	400				8100	neg			14	
2I	2,5-dimethyl-2,4-hexadiene*	645				5000	2010 ± 140	1.28 ± 0.09	2570	15	7–15
2J	1,4-cyclohexadiene*		340	440	0.96		279 ± 17	0.46 ± 0.03	130	10	5–12
	1,4-cyclohexadiene		345	445	0.96		cur			450	
	1,4-cyclohexadiene[c]		350	444	1.13		2150 ± 110	0.06 ± 0.01	130		
2K	1,5-cyclooctadiene	420				7100	cur			10	
2L	hexamethyl Dewar benzene*		475	535	0.88						
3A	1-pentyne	335 sh								20	
3B	2-pentyne	355					cur			20	
3C	1-hexyne	335 sh									
3D	2-hexyne	365					305 ± 54	0.50 ± 0.09	150	1	2–4
	2-hexyne	365					cur			20	
3E	3-hexyne	365					368 ± 84	0.32 ± 0.07	120	1	1–3
	3-hexyne	365					cur			20	
3F	2,4-hexadiyne	405				5700	2120 ± 80	0.34 ± 0.01	720	67	7–15
3G	1,7-octadiyne	330 sh									
4A	benzene	385				5800	3560 ± 660	0.12 ± 0.02	430	10	1–3
	benzene	385				5800	2630 ± 260	0.17 ± 0.02	450	40	3–7
	benzene	385				5800	4450 ± 240	0.10 ± 0.01	450	160	4–8
	benzene	385				5800	5150 ± 290	0.10 ± 0.01	410	622	6–13
	benzene (composite of four above)						4410 ± 110	0.10 ± 0.01	440		1–16
	benzene[b]	385				5800	3570	0.10	360		
	benzene[e]	385				5900	3310 ± 430	0.11 ± 0.01	360		
	benzene[f]	385				5800	736 ± 56	0.67 ± 0.05	490	15	9–15
	benzene[g] (in $CHCl_3$)	391					2900 ± 50	0.25 ± 0.01	730		
4B	benzene-d_6	390				6000	1600 ± 100	0.29 ± 0.02	460	29	4–8
	benzene-d_6	385				6200	cur			429	
5A	toluene	410				6500	2760 ± 480	0.28 ± 0.05	770	11	2–5
	toluene	410				6500	3190 ± 140	0.24 ± 0.01	770	35	4–8
	toluene	410				6800	3800 ± 240	0.20 ± 0.01	760	150	6–13
	toluene	410				6800	3080 ± 90	0.26 ± 0.01	800	615	14–27
	toluene (composite of four above)						3890 ± 80	0.19 ± 0.01	740		1–22
	toluene[b]	406				6800	3300	0.20	660		
	toluene[e]	410				6500	1410 ± 130	0.56 ± 0.05	790	10	3–9
	toluene[f]	405	*395*	*425*	*1.08*	6800	2680	0.26	700		
5B	ethylbenzene	412				6600	1800 ± 210	0.33 ± 0.04	590	1	<1
	ethylbenzene	415				6500	1680 ± 310	0.37 ± 0.07	620	10	3–7
	ethylbenzene	410				6500	cur			390	
5C	*n*-propylbenzene	415				6600	2950 ± 350	0.19 ± 0.02	560	20	2–5
	n-propylbenzene	410				6800	2020 ± 130	0.30 ± 0.02	610	272	11–23
	n-propylbenzene	410				6700	cur			334	
5D	isopropylbenzene	413				6500	3630 ± 390	0.10 ± 0.01	360	100	3–7
	isopropylbenzene	413				6800	10100 ± 1100	0.04 ± 0.01	400	527	3–7
	isopropylbenzene[h]	418									
5E	*tert*-butylbenzene	415				6800	8800 ± 2100	0.03 ± 0.01	300	100	1–3
	tert-butylbenzene[i] (in $CHCl_3$)	420	*402*	*453*	*0.84*						
5F	1,2-dimethylbenzene	435				6500	3950 ± 100	0.55 ± 0.02	2170	647	21–39
	1,2-dimethylbenzene[b]	430				6400	3860	0.37	1430		
	1,2-dimethylbenzene[f]		*419*	*453*	*0.94*	6400	2510 ± 180	0.67 ± 0.05	1680		
5G	1,3-dimethylbenzene	435				6100	2570 ± 110	0.66 ± 0.03	1700	200	15–30
	1,3-dimethylbenzene	435				6200	3030 ± 80	0.57 ± 0.02	1730	860	23–41
	1,3-dimethylbenzene[b]	440				6400	3300	0.33	1100		
5H	1,4-dimethylbenzene		415	460		8400	2980 ± 120	0.41 ± 0.02	1220	185	9–19
	1,4-dimethylbenzene		415	460	0.95	8600	2880 ± 20	0.45 ± 0.01	1300	694	17–32
	1,4-dimethylbenzene[b]		415	460	0.96		2650	0.43	1140		
	1,4-dimethylbenzene[f]		*388*	*466*	*1.61*		1710 ± 40	0.73 ± 0.02	1250		
	1,4-dimethylbenzene[i] (in $CHCl_3$)	425	*408*	*490*	*0.96*						

Table I (Continued)

code	donor molecule	λ_{max}, nm	λ_1, nm	λ_2, nm	A_2/A_1	$\Delta\nu_{1/2}$, cm^{-1}	ϵ_{max}, L/(mol cm)	K, L/mol	ϵK	C_D/C_T	% satn
5I	1,4-diethylbenzene		418	465	0.93	8300	4190 ± 500	0.16 ± 0.02	670	68	3–8
5J	1,4-di-*tert*-butylbenzene		400	417	1.02	7300	cur			1	
	1,4-di-*tert*-butylbenzene[i] (in CHCl$_3$)	427	*426*	*521*	*0.47*						
5K	1,2,3-trimethylbenzene	465				5800	3560 ± 760	1.29 ± 0.28	4590	1/16	4–8
	1,2,3-trimethylbenzene	470				5300	1990 ± 130	2.27 ± 0.15	4520	20	8–17
	1,2,3-trimethylbenzene	465				5600	cur			109	
5L	1,2,4-trimethylbenzene	450				7200	2750 ± 170	1.24 ± 0.07	3410	20	6–12
	1,2,4-trimethylbenzene	455				7300	cur			860	
5M	1,2,4-triethylbenzene	465				7300	714 ± 37	1.70 ± 0.09	1210	1	1–5
	1,2,4-triethylbenzene	465				7300	cur			92	
5N	1,3,5-trimethylbenzene	465				5600	2460 ± 160	1.56 ± 0.10	3840	20	9–18
	1,3,5-trimethylbenzene	465				5600	3360 ± 120	1.07 ± 0.04	3600	182	14–28
	1,3,5-trimethylbenzene	460				5600	4440 ± 140	0.77 ± 0.03	3420	1110	23–41
	1,3,5-trimethylbenzene[b]	460				5600	3120	1.03	3210		
	1,3,5-trimethylbenzene[f]	461					2600 ± 350	1.33 ± 0.18	3460		
5O	1,3,5-triethylbenzene	473				5600	4770 ± 840	0.27 ± 0.05	1290	100	4–10
5P	1,3,5-tri-*tert*-butylbenzene	450sh					neg			9	
5Q	1,2,3,4-tetramethylbenzene	495				5500	2300 ± 70	4.43 ± 0.14	10200	1/20	13–26
	1,2,3,4-tetramethylbenzene	490				5800	cur			19	
5R	1,2,3,5-tetramethylbenzene (85%)	495				5900	2420 ± 50	3.81 ± 0.08	9220	1/20	11–23
5S	1,2,4,5-tetramethylbenzene	480				7400	1920 ± 70	4.27 ± 0.16	8200	1/20	12–25
	1,2,4,5-tetramethylbenzene[b]	480					2075	3.37	7000		
	1,2,4,5-tetramethylbenzene[f]		*441*	*521*	*1.58*		2960 ± 30	2.40 ± 0.02	7100		
5T	pentamethylbenzene	510				5800	5220 ± 220	4.49 ± 0.20	23400	41	11–23
	pentamethylbenzene[b]	520				5800	3270	7.39	25500		
	pentamethylbenzene[f]		*507*	*546*	*0.77*		3920 ± 220	6.67 ± 0.37	26200		
5U	hexamethylbenzene	540				5400	4110 ± 140	20.74 ± 0.74	85200	20	18–33
	hexamethylbenzene[b]	545				5500	4390	16.77	73600		
	hexamethylbenzene[f]	545				5300	4240 ± 110	19.25 ± 0.50	81600		
5V	hexaethylbenzene	540				8400	neg			9	
5W	cyclopropylbenzene	405	*400*	*480*	*0.83*	9300	3680 ± 320	0.14 ± 0.01	520	20	1–4
	cyclopropylbenzene		405	460 sh	0.87	9500	3290 ± 250	0.16 ± 0.01	530	368	8–18
	cyclopropylbenzene[h]	480									
5X	allylbenzene	405				7100	1670 ± 90	0.28 ± 0.02	470	20	4–8
6A	1,2-diphenylethane	410				6700	880 ± 40	1.20 ± 0.06	1060	10	8–18
	1,2-diphenylethane	410				6700	2370 ± 260	0.40 ± 0.04	950	58	6–13
6B	1,2-diphenylcyclopropane		400	475 sh	0.68		1760 ± 70	0.50 ± 0.02	880	20	5–11
6C	9,10-dihydroanthracene	435					1480 ± 140	1.09 ± 0.11	1610	1/10	3–6
	9,10-dihydroanthracene	435					cur			20	
6D	iminobibenzyl		415	810	1.48		1940 ± 70	2.78 ± 0.10	5390	20	10–20
6E	[2.2]paracyclophane	515				6200	2110 ± 230	2.60 ± 0.29	5490	1/16	7–14
	[2.2]paracyclophane[j]	521									
6F	biphenyl		390	495	0.88		1290 ± 160	0.37 ± 0.05	480	19	4–9
	biphenyl		390	495	0.88		2750 ± 270	0.17 ± 0.02	470	230	7–15
	biphenyl[b]	500					1450	0.17	250		
	biphenyl[g] (in CHCl$_3$)	505					1050 ± 50	0.73 ± 0.02	770		
6G	fluorene		415	565	1.42		1490 ± 90	1.12 ± 0.07	1670	15	6–13
	fluorene		415	565	1.42		1480 ± 40	1.11 ± 0.03	1640	125	17–30
	fluorene[b]		416	570	1.35		1430	1.08	1540		
	fluorene[g] (in CHCl$_3$)		419	567			2000 ± 50	1.44 ± 0.08	2880		
6H	9,10-dihydrophenanthrene		425	560	1.10		960 ± 40	1.01 ± 0.04	970	14	5–12
	9,10-dihydrophenanthrene		425	565	1.09		1180 ± 50	0.85 ± 0.04	1000	82	14–27
	9,10-dihydrophenanthrene[h]		425	566							
6I	carbazole[e]		385	600	3.24	6200	3860 ± 230	1.46 ± 0.09	5640	1/20	8–13
	carbazole[g] (in CHCl$_3$)	605					2900 ± 50	5.12 ± 0.13	14850		
7A	styrene		395	480	1.17		674 ± 61	0.69 ± 0.06	470	15	8–17
	styrene		395	475	1.13		2410 ± 190	0.18 ± 0.01	430	76	5–10
	styrene[g] (in CHCl$_3$)	485					1250 ± 50	0.65 ± 0.01	810		
	styrene[k] (in CHCl$_3$)		390	487							
7B	2-methylstyrene	435	*425*	*475*	*0.74*	7600	251 ± 6	2.82 ± 0.01	710	20	26–42
7C	3-methylstyrene		440	490	1.02		880 ± 70	1.02 ± 0.08	900	20	11–21
	3-methylstyrene		440	487	1.02		2130 ± 90	0.39 ± 0.02	830	46	6–13
7D	4-methylstyrene		395	525	1.38		340 ± 9	2.66 ± 0.08	900	30	26–43
7E	2,4-dimethylstyrene*		435	525	1.07		cur			20	
7F	2,5-dimethylstyrene	475	*460*	*540*		7300	820 ± 70	2.34 ± 0.19	1910	1/10	14–25
	2,5-dimethylstyrene	475				7500	cur			20	
7G	2,6-dimethylstyrene	465	*455*	*480*		5700	1690 ± 90	1.15 ± 0.06	1940	20	8–16
7H	2,4,6-trimethylstyrene	480	*455*	*505*		6500	1650 ± 50	2.33 ± 0.07	3850	20	15–29
7I	2,3,4,5,6-pentamethylstyrene	540				5300	4720 ± 260	5.22 ± 0.29	24600	20	9–18
	2,3,4,5,6-pentamethylstyrene	540				5400	4400 ± 160	5.31 ± 0.21	24600	88	17–33
7J	α-methylstyrene		400	490	1.04		285 ± 18	1.38 ± 0.09	390	26	20–36
7K	*trans*-β-methylstyrene		400	530	1.52		cur			28	
7L	1-phenyl-1-cyclohexene		400	560	1.24		283 ± 15	2.26 ± 0.12	640	1/10	8–14
	1-phenyl-1-cyclohexene		400	560	1.24		cur			20	
7M	β,β-dimethylstyrene		400	545	1.10		1200 ± 110	0.35 ± 0.03	420	20	4–8

Table I (Continued)

code	donor molecule	λ_{max}, nm	λ_1, nm	λ_2, nm	A_2/A_1	$\Delta\nu_{1/2}$, cm^{-1}	ϵ_{max}, L/(mol cm)	K, L/mol	ϵK	C_D/C_T	% satn
7N	indene		420	540	1.24		799 ± 65	1.60 ± 0.13	1280	1/10	5–11
	indene		420	540	1.24		curr			20	
	indene[g] (in CHCl$_3$)		430	542			1350 ± 50	1.63 ± 0.04	2200		
7O	1,2-dihydronaphthalene		425	565	1.17		508 ± 63	1.64 ± 0.20	830	1/10	5–11
	1,2-dihydronaphthalene		425	560	1.17		cur			44	
7P	*m*-diisopropenylbenzene	505				6900	357 ± 10	1.70 ± 0.05	610	20	18–33
	m-diisopropenylbenzene	505				6800	267 ± 11	2.35 ± 0.13	630	65	36–55
7Q	*p*-diisopropenylbenzene*		410 sh	575		5000	76 ± 1	7.26 ± 0.13	550	20	54–72
8A	1,1-diphenylethylene		395 sh	510			483 ± 63	0.53 ± 0.07	260	10	5–9
	1,1-diphenylethylene		400 sh	507			cur			93	
	1,1-diphenylethylene[k]		390	522							
8B	*cis*-1,2-diphenylethylene		390	530	0.79		2620 ± 260	0.18 ± 0.02	470	15	3–7
	cis-1,2-diphenylethylene		390	530	0.79		2350 ± 210	0.18 ± 0.02	420	97	5–10
	cis-1,2-diphenylethylene[k]		390	547							
	cis-1,2-diphenylethylene[l]		390	532			280	1.68	470		
	cis-1,2-diphenylethylene[m]		403	535							
8C	*trans*-1,2-diphenylethylene		400 sh	595		5200	1160 ± 70	0.93 ± 0.06	1080	20	8–15
	trans-1,2-diphenylethylene		400 sh	595		5100	3340 ± 290	0.29 ± 0.03	970	92	5–11
	trans-1,2-diphenylethylene[k]		377	608							
	trans-1,2-diphenylethylene[l]		390	595			720	1.35	970		
	trans-1,2-diphenylethylene[m]		395	602							
8D	*N*-benzylideneaniline	495					228 ± 20	3.08 ± 0.28	700	1/10	10–20
	N-benzylideneaniline	495					400 ± 51	1.79 ± 0.23	720	1	2–6
	N-benzylideneaniline	495					648 ± 39	1.12 ± 0.06	730	20	12–22
8E	1,1-di-*o*-tolylethylene	435	425	510	0.70	8100	766 ± 37	0.69 ± 0.03	530	11	7–14
8F	1,1-di-*p*-tolylethylene		400 sh	565			149 ± 3	3.14 ± 0.06	470	20	33–52
8G	iminostilbene	780					1110 ± 90	7.03 ± 0.66	7800	20	18–30
8H	triphenylethylene		400 sh	595		5500	1570 ± 370	0.29 ± 0.07	460	20	3–6
	triphenylethylene[k]		390	623							
8I	tetraphenylethylene	600					622 ± 110	0.27 ± 0.05	170	1	1–2
	tetraphenylethylene[b]	610					67	0.92	60		
	tetraphenylethylene[k]		390	650							
8J	1,4-diphenyl-1,3-butadiene*	675					714 ± 75	2.19 ± 0.23	1560	1/9	7–15
8K	1,6-diphenyl-1,3,5-hexatriene*	775					cur			1/10	
8L	1,8-diphenyl-1,3,5,7-octatetraene*	>750								1/10	
8M	1,1,4,4-tetraphenyl-1,3-butadiene	730					213 ± 32	1.80 ± 0.27	380	1/6	9–12
9A	phenylacetylene	420	*370*	*435*	*1.27*		1250 ± 140	0.21 ± 0.02	260	15	3–7
	phenylacetylene	420					3950 ± 730	0.06 ± 0.01	240	149	3–7
9B	1-phenyl-1-propyne		365	475	1.29		739 ± 21	0.81 ± 0.02	600	14	10–17
	1-phenyl-1-propyne		365	475			cur			121	
9C	diphenylacetylene		365 sh	520		5600	934 ± 58	0.72 ± 0.05	670	21	10–17
	diphenylacetylene		365 sh	525	1.05	5800	1740 ± 110	0.36 ± 0.02	630	100	8–17
9D	diphenylbutadiyne		375 sh	510			448 ± 18	1.24 ± 0.05	560	10	13–20
	diphenylbutadiyne		375 sh	508		6300	4040 ± 340	0.11 ± 0.01	560	460	2–5

[a] Reference 15. [b] Reference 1. [c] Reference 3. [d] Reference 18. [e] Reference 4. [f] Reference 5. [g] Cooper, A. R.; Crowne, C. W. P.; Farrell, P. G. *Trans. Faraday Soc.* **1966**, *62*, 18–28. [h] Reference 31. [i] Holder, D. D.; Thompson, C. C. *J. Chem. Soc., Chem. Commun.* **1972**, *277*–279. [j] Reference 37. [k] Bendig, J.; Dobslaw, B.; Kreysig, D.; Sauer, J. *J. Prakt. Chem.* **1976**, *318*, 616–628. [l] Reference 46. [m] Matsuo, T.; Aiga, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 271–274.

modifications in structural groups.

The ratios of the concentrations of stock solutions of donor, C_D, and TCNE, C_T, are given in column 11. When C_D is larger than C_T, the ratio is reported as an integer; when TCNE is used in excess, C_D/C_T is reported as a fraction. Finally, the saturation fraction range times 100, percent s, is given in column 12.

1. **Cycloalkanes.** TCNE complexes of a highly strained alkane ring system are compared with those of an unstrained system.

a. **Methylcyclopropanes.** The absorbance spectra of **1A**-, **1B**-, and **1C**-TCNE appear as broad featureless bands that rise steeply from about 500 nm to the TCNE absorbance cutoff at 300–325 nm. The Scott lines have small gradients; that of **1A**-TCNE is negative, whereas the Scott lines of **1B**- and **1C**-TCNE yield apparent K values of 0.04 L/mol. This value corresponds to an actual K_{XY} of about 0.2 L/mol when corrected for solvent complexation by using eq 4. It is interesting to note that Prue[13] obtained a value of 0.2 L/mol for K_{XY} of CCT complexes using a theoretical model. In view of the large uncertainties in the K value and the small saturation fraction ranges (1–5%) involved, the best that can be said is that complexes of TCNE with methylcyclopropanes are very weak and that the observed spectra probably arise from CCT interactions. The ϵK values of **1B**- and **1C**-TCNE at 30 and 12 are the lowest values obtained in this study.

The wavelengths at one-half maximum absorbance for the spectral bands of **1A**-, **1B**-, and **1C**-TCNE are 350, 385, and 425 nm, respectively, indicating that the CT band energies decrease with increasing methyl substitution of the cyclopropane ring. This trend is consistent with the well-known tendency of methyl groups to donate electrons to carbon atoms that have sp or sp^2 hybridization or that are members of highly strained rings. Although the IE values of **1A**, **1B**, and **1C** have not been reported, Heilbronner, et al.[14] have determined the IEs of the closely related 1,2-disubstituted cyclopropane derivative bicyclo[4.1.0]heptane from its PE spectrum. They assigned the IEs at 9.46 and 10.01 eV for this compound to the in-plane e_s and e_a Walsh orbitals, which values when substituted into eq 1′ correspond to CT bands with λ_{max} 365 and 325 nm. These results suggest that the spectra of TCNE

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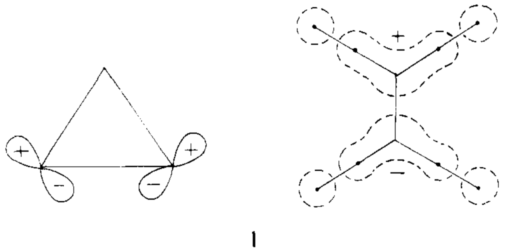
(13) Prue, J. E. *J. Chem. Soc.* **1965**, 7534–7535.

(14) Heilbronner, E.; Gleiter, R.; Hoshi, T.; de Meijere, A. *Helv. Chim. Acta* **1973**, *56*, 1594–1604.

complexes of **1A**, **1B**, and **1C** likewise arise from $e_s \rightarrow \pi^*$ and $e_a \rightarrow \pi^*$ transitions between the donor and acceptor moieties, since the absorbance bands of these complexes bracket the calculated CT energies.

Optimum overlap between the donor and acceptor orbitals is expected to occur when the cyclopropane ring is parallel to the plane of TCNE as shown in structures I and II. Since the substituents on the cyclopropane ring strongly hinder effective contact between the donor–acceptor pair, it is not surprising that the calculated association constants for these complexes are 1–2 orders of magnitude lower than usual for CT complexes in which the binding sites are not hindered.



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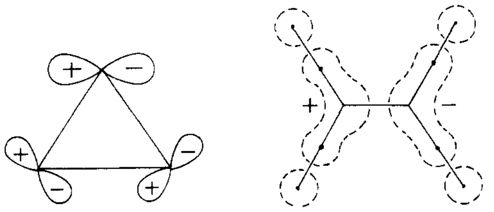

II

b. Adamantanes. Traven et al.[15] reported the formation of CT complexes of several σ-donor hydrocarbons with TCNE. A mixture of **1D** and TCNE in chloroform was described as having a band with a maximum at 355 nm. Our spectrum of **1D**–TCNE consists of a broad shoulder with λ 365 nm at one-half maximum band height. Analysis of the spectra yields values of K and ϵK that are somewhat greater than those obtained for the methylcyclopropane complexes. The characteristics of **1D**- and **1E**–TCNE are quite similar, indicating that the two methyl groups on **1E** have little effect on the interaction of TCNE with the adamantane cage. The results of our work are in accord with those obtained from the studies of PE spectra of **1D** and some of its methyl derivatives by Worley et al.[16] First, the IE of **1D** at 9.44 eV corresponds to a CT band with λ_{max} 370 nm, which is in good agreement with our value of 365 nm for the half-absorbance value. Second, the substitution of a methyl group has only a slight effect on the orbital energies of the adamantyl cage.

c. Summary and Conclusions. (1) The methylcyclopropanes and TCNE form weak CCT complexes. Their instability is due primarily to the methyls which hinder effective overlap of the donor and acceptor orbitals. The adamantanes form relatively stable CT complexes with TCNE, indicating effective overlap between the donor orbitals and π^* acceptor orbitals.

(2) The half-height wavelengths of the bands for the methylcyclopropane/TCNE systems increase by 35–40 nm per methyl substituted on the cyclopropane ring, indicating that methyl carbons are electron-releasing with respect to carbons in strained alkane rings. The half-height wavelengths for the adamantane–TCNE complexes are invariant with methyl substitution, indicating that methyl groups are not electron-releasing with respect to the carbons in relatively unstrained ring systems. These observations support the supposition that carbons in strained rings have more s character (are less electronegative) than the sp^3 carbons in methyl groups.

(3) The good correlation between the half-height wavelengths of the bands of the cyclopropane– and adamantane–TCNE systems with the IEs of the corresponding cyclopropane–Walsh and adamantane–σ orbitals supports the supposition that the absorbances of the TCNE complexes of the methylcyclopropanes and the adamantanes arise from CT transitions between the cycloalkane and TCNE moieties.

2. Alkenes. The most extensive study of alkene–TCNE complexes to date is that of Haselbach and Rossi,[3] who reported both spectroscopic properties and association constants for CT complexes of five cyclic monoalkenes and seven cyclic dienes and trienes. Other studies include those of Merrifield and Phillips[1] on cyclohexene–TCNE and of Ponec, Chvalovsky, and co-workers[17,18] on TCNE complexes of two cyclic and two acyclic monoalkenes. Ponec et al. determined that the absorbances of alkene–TCNE complexes arise from a $\pi_e \rightarrow \pi^*$ electron transfer that originates in the ethylenic π orbital (π_e) of the alkene molecule and terminates in the LUMO (π^*) of the TCNE.

a. Monoalkenes. Ponec and Chvalovsky[17] reported λ_{max} values of 337 and 350 nm for $CH_2{=}CHCMe_3$—TCNE and $CH_2{=}CHCH_2CMe_3$—TCNE. We report values of 355, 410, 415, 415, 465, and 535 nm for mixtures of TCNE and the hexenes **2A**, **2B**, **2C**, **2D**, **2E**, and **2F** in DCM. The value of λ_{max} increases by about 60 nm per alkyl carbon atom attached to the ethylenic carbons in this sequence. A plot of λ_{max} versus n, where n is the degree of alkyl substitution of the ethylenic group (i.e., the number of alkyl carbons attached to ethylenic carbons), yields a line with the equation

$$\lambda_{max} = \lambda_0 + Bn = 292 + 60.6n \qquad (6)$$

Here λ_0 is the hypothetical λ_{max} for ethylene–TCNE, and B is the increment in λ for each carbon bound to the ethylenic carbons; the correlation coefficient is 0.997. When the IE values of the π orbitals of the cognate acyclic alkenes[19] **2A**, **2B**, **2C**, and **2F** at 9.48, 8.97, 8.97, and 8.27 eV together with that of the cyclic alkene[20] **2D** at 9.12 eV are substituted into eq 1′, they yield CT energies for the corresponding TCNE complexes equivalent to 365, 415, 415, 513, and 399 nm. These values are generally in good agreement with the experimental values above (355, 410, 415, 535, and 415 nm), indicating that the absorbances of the TCNE complexes of the hexanes do indeed arise from $\pi_e \rightarrow \pi^*$ transitions. The high degree of correlation between λ_{max} and n expressed in eq 6 is not surprising in view of the fact that Masclet et al.[19] showed that the IEs of a set of alkenes decreases in seriatim with increasing n. It is interesting to note that the IE of ethylene calculated from eq 6 and 1′ (10.53 eV) is almost identical with the experimental value (10.52 eV) determined by Masclet et al.[19]

Merrifield and Phillips[1] and Haselbach and Rossi[3] reported ϵ values of 4760 and 2000 and K values of <0.01 and 0.03 L/mol for **2D**–TCNE. However, out attempts to analyze this system using stock solutions with a 20-fold

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[15] Traven, V. F.; Donyagina, V. F.; Fedotov, N. S.; Evert, G. V.; Stepanov, B. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1976**, *46*, 2738–2739; *Zh. Obshch. Khim.* **1976**, *46*, 2761.

[16] Worley, S. D.; Mateescu, G. D.; McFarland, C. W.; Fort, R. C.; Sheley, C. F. *J. Am. Chem. Soc.* **1973**, *95*, 7580–7586.

[17] Ponec, R.; Chvalovsky, V. *Coll. Czech. Chem. Commun.* **1973**, *38*, 3845–3851.

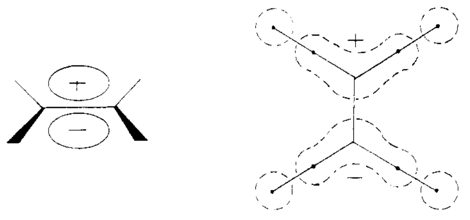
[18] Ponec, R.; Chvalovsky, V.; Cernysev, E. A.; Komarenkova, N. G.; Baskirova, S. A. *Coll. Czech. Chem. Commun.* **1974**, *39*, 1177–1184.

[19] Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois, J. *J. Electron Spectrosc.* **1973**, *2*, 225–237.

[20] Bischof, P.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 1677–1682.

excess of **2D** yielded Scott lines with distinct curvature. We obtained a similar result in our analysis of **2B**–TCNE. Scott analyses of **2A**–, **2C**–, and **2F**–TCNE yield lines with only slightly positive slopes and with very large relative uncertainties; here K values range from 0.03 to 0.05 L/mol and percent saturation values range from only 1 to 5. The Scott lines of **2E**–TCNE and the nonconjugated dienes **2G**– and **2H**–TCNE are negative, indicating that the interaction of isolated unstrained ethylenic groups with TCNE is extremely weak and results in the formation of CCT complexes. The low solubility of TCNE precluded studies of alkene–TCNE systems using excess TCNE. Reports of ϵ and K values from such systems must be regarded with caution in the absence of information on the saturation fraction range.

The magnitude of the K values of monoalkene–TCNE complexes is expected to depend upon the effectiveness of the overlap between the π_e and π^* orbitals of the ethylenic group and TCNE. The configuration of optimum overlap, that in which the plane of the atoms attached to the doubly bonded carbons in the alkene is perpendicular to the plane of TCNE (structure III), is strongly hindered by the projecting atoms. Consequently K values for alkene–TCNE complexes tend to be very small.



III

b. Dienes. The λ_{max} values for the TCNE complexes of the 1,5-dienes **2G**–TCNE (345 nm) and **2H**–TCNE (400 nm) are 10 nm lower than the λ_{max} values for **2A**–TCNE (355 nm) and **2B**–TCNE (410 nm), which have ethylenic groups with the same degrees of alkyl substitution. This indicates that there is no appreciable intramolecular through-space conjugation between the double bonds in these 1,5-dienes and that TCNE interacts with the ethylenic groups in these molecules as if they were isolated from one another.

The situation is quite different in the case of the complex of the conjugated 2,4-diene **2I**. While conjugated dienes such as 1,3-butadiene undergo rapid Diels–Alder additions with TCNE,[21] the reaction of the tetramethylbutadiene, **2I**, is slow enough to allow for the characterization of **2I**–TCNE. The high values of λ_{max} (645 nm) and K (1.28 L/mol) compared to complexes of TCNE with nonconjugated double bonds (Figure 1) reflects both the lower IE and the greater accessibility of the π orbitals in the delocalized system.

Haselbach and Rossi[3] reported that TCNE complexes of homoconjugated cyclic dienes such as **2J** had two absorbance bands, which they ascribed to CT interactions originating from the $b_2(\pi)$ and $a_1(\pi)$ orbitals of the diene. They also reported ϵ and K values of 2150 and 0.06 L/mol for **2J**–TCNE. We attempted to characterize this complex using stock solutions in which C_D/C_T ratios were 10 and 450. The first system yields a Scott line with a correlation coefficient of 0.983 but with possible marginal curvature. We report ϵ and K values of 279 and 0.46 L/mol for the **2J**–TCNE system. It is interesting to note that our first ϵK value for **2J**–TCNE (130) is identical with that of Haselbach and Rossi.[3] Our second determination, using a large excess of diene over TCNE, yields a distinctly curved line, indicating that this system probably contains a significant concentration of 2:1 complexes.

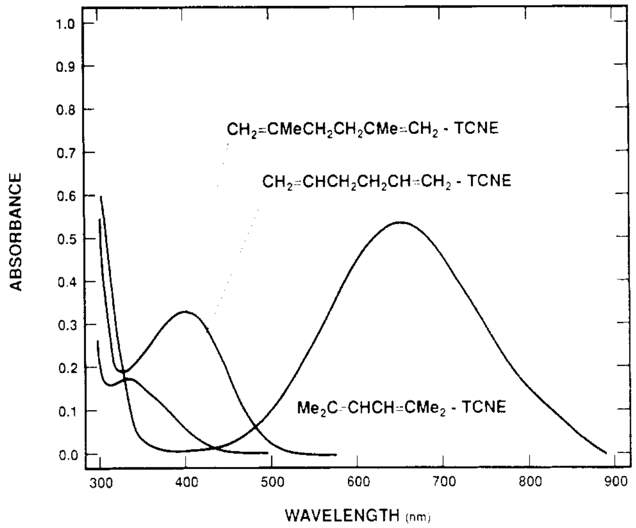


Figure 1. Spectra of hexadiene–TCNE complexes.

Mixtures of TCNE with the nonconjugated cyclic diene **2K** exhibit a single band with λ_{max} 420 nm and yield a curved Scott line. The similarity in behavior of this system with those of **2C**– and **2D**–TCNE indicate that there is no homoconjugation in **2K**. This interpretation is in accord of that of Batich et al.,[22] who observed that **2K** has a single band in its PE spectrum at 9.06 eV corresponding to a π-orbital ionization. When this value is substituted into eq 1′ it yields a λ_{max} of 405 nm, which is in good agreement with the experimental value of 420 nm.

A mixture of TCNE and **2L** (hexamethyl Dewar benzene or 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene) in DCM exhibited a purple color that intensified on standing. The spectrum of the freshly mixed solution had a sharp peak at 475 nm with a weak shoulder at 450 nm and a broad absorbance band with λ_{max} 535 nm. The Scott analysis of the system yielded a strongly curved line. It appears as if a complex **2L**–TCNE forms but that its formation is accompanied by an irreversible reaction. The system is further complicated by the photosensitivity of **2L**.

c. Summary and Conclusions. (1) TCNE forms CCT complexes with alkenes in DCM solutions; the spectral absorbance bands of these complexes arise from a $\pi_e \rightarrow \pi^*$ transition. The instability of the complexes is due to the orientation of the hydrogens which hinder effective overlap between the donor and acceptor orbitals.

(2) The λ_{max} values of a series of alkylethylene–TCNE complexes increases by 60 nm per alkyl group attached to the ethylenic carbons, indicating that such alkyl groups donate electrons additively to adjacent π orbitals.

(3) Complexes of TCNE with nonconjugated dienes have characteristics that are similar to those of monoalkene–TCNE complexes, whereas TCNE complexes of conjugated butadienes have larger λ and K values.

3. Alkynes. No previous reports of alkyne–TCNE complexes have appeared in the literature.

a. Monoalkynes. We observed that the spectra of mixtures of TCNE with the monoalkylethynes **3A** and **3C** in DCM exhibit very weak shoulders with a half-height at

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(21) Middleton, W. G.; Heckert, R. E.; Little, E. L.; Krespan, C. G. *J. Am. Chem. Soc.* **1958**, *80*, 2783–2788.

(22) Batich, C.; Bischof, P.; Heilbronner, E. *J. Electron Spectrosc.* **1972/1973**, *1*, 333–353.

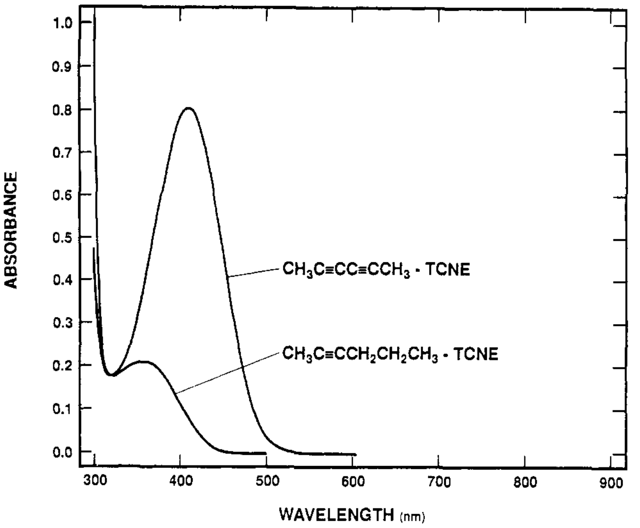

Figure 2. Spectra of hexyne–TCNE complexes.

335 nm. When the IE values of the π orbitals of **3A** and **3B**, 10.10 and 10.07 eV,[23] are substituted into eq 1′, they yield λ_{max} values corresponding to 318 and 320 nm, which indicates that the shoulders are due to CT absorbances of **3A**- and **3C**–TCNE. The spectra of complexes of TCNE with dialkylethynes **3B**, **3D**, and **3E** (Figure 2) consist of bands with maxima at 355, 365, and 365 nm. When the IE values of the orbitals of these compounds, 9.44, 9.39, and 9.32 eV,[23] are substituted into eq 1′, they yield λ_{max} values of 368, 375, and 379 nm for the corresponding complexes **3B**–, **3D**–, and **3E**–TCNE, indicating that these bands arise from $\pi_e \rightarrow \pi^*$ transitions in the complexes which originate in the π orbitals (π_e) of the alkyne molecule. A comparison of λ_{max} values of mono- and dialkylethyne complexes of TCNE indicates that the substitution of a second alkyl group on an ethyne carbon gives rise to a λ_{max} increase of 20–30 nm.

Scott analyses of **3B**–, **3D**–, and **3E**–TCNE yield strongly curved lines when the stock solutions contain excess alkyne, indicating the formation of D_2T complexes. Consequently the characteristics of **3D**–TCNE and **3E**–TCNE were determined by using the Foster–Matheson procedure,[7] which in these cases yields K values with large uncertainties because of the low saturation ranges covered. The K values of the two complexes, 0.50 and 0.32 L/mol, are about 10-fold larger than those obtained for corresponding alkene–TCNE complexes. This may be due to the absence of steric hindrance to the effective overlap of the π_e and π^* orbitals of the alkynes and TCNE.

b. Dialkynes. The spectrum of mixtures of TCNE with the 2,4-diyne **3F** (Figure 2) consists of a band with λ_{max} 405 nm, which indicates that there is conjugation between the triple bonds in **3F**. This interpretation is supported by the PES studies of **3F** by Broglie et al.,[24] who attributed a peak at 8.91 eV to an orbital formed by the conjugation of the triple bonds. The IE value of 8.91 eV when substituted into eq 1′ yields a λ_{max} value of 420 nm for **3F**–TCNE, which compares favorably with the experimental value of 405 nm.

The spectrum of a mixture of TCNE with **3G** consists of a shoulder that rises steeply at 375 nm; this indicates that there is no conjugative interaction between the triple bonds in **3G**.

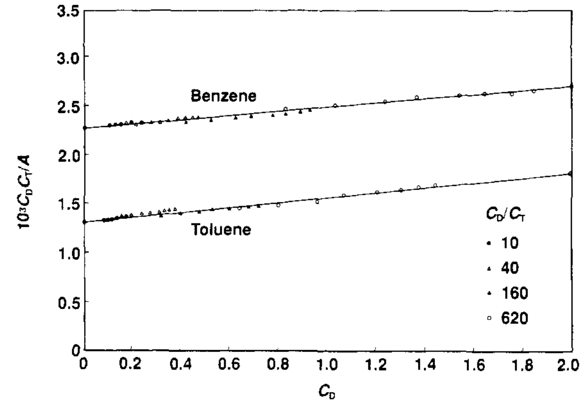

Figure 3. Scott graphs of benzene–TCNE and toluene–TCNE systems.

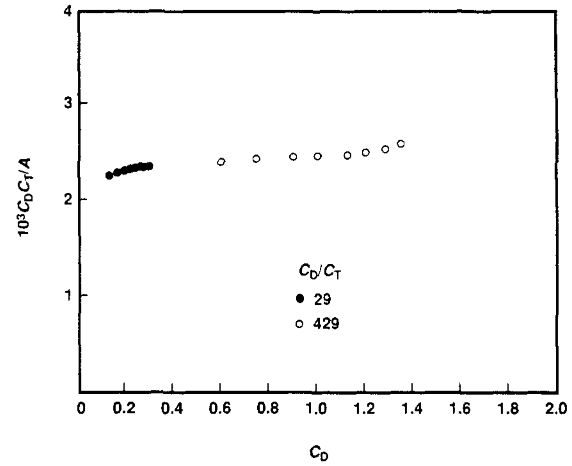

Figure 4. Scott graphs for benzene-d_6–TCNE systems.

c. Summary and Conclusions. (1) Alkynes form CT complexes with TCNE that exhibit absorbance bands that arise from $\pi_e \rightarrow \pi^*$ transitions.

(2) The substitution of a second alkyl on an ethyne group increases λ_{max} of the ethyne–TCNE complex by 20–30 nm.

(3) The K values of alkyne–TCNE complexes (0.3–0.5 L/mol) are about an order of magnitude higher than those of corresponding alkene–TCNE complexes, indicating that there is less steric interference in a triple bond–TCNE interaction.

(4) The λ_{max} value of **3F** at 405 nm indicates that there is conjugation between the triple bonds.

4. Benzene and Benzene-d_6. We report the results of investigations of the **4A**–TCNE and **4B**–TCNE systems that indicate that ϵ and K values do not vary with the concentration ratios of the reagent solutions.

a. Benzene. Merrifield and Phillips[1] and Rossi et al.[4] reported ϵ and K values for **4A**–TCNE of 3570 and 0.10 L/mol and 3310 and 0.11 L/mol in DCM. The data for the Scott graph for our study of the **4A**/TCNE system are drawn from four runs that covered the entire range of feasible dilution ratios. The results of each run and the composite of the four runs are shown in Table I and Figure 3. The locus of the 32 points is a line with $r = 0.982$. The ϵ and K values are in good agreement with previously reported values, and the linearity indicates that there are neglible quantites of D_2T species in the saturation range covered in this study. Unfortunately the low K value precludes the experimental feasibility of extending the saturation range into the optimum region prescribed by Deranleau.[11]

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[23] Carlier, P.; Dubois, J. E.; Masclet, P.; Mouvier, G. *J. Electron Spectrosc.* **1974**, *7*, 55–67.

[24] Broglie, F.; Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1973**, *56*, 2171–2178.

Table II. Selected Values of Spectral Characteristics and Association Constants for Methylbenzene–TCNE Complexes in Dichloromethane at 21 °C

code	n^a	λ_{max}, nm	ϵ, L/(mol cm)	K, L/mol	ϵK
4A	0	385	4410	0.10	440
5A	1	405	3890	0.19	740
5F	2	435	3950	0.55	2170
5G	2	435	2570	0.66	1700
5H	2	435	2880	0.45	1300
5K	3	465	3560	1.29	4590
5L	3	455	2750	1.24	3410
5N	3	465	2460	1.56	3840
5Q	4	495	2300	4.43	10200
5R	4	495	2420	3.81	9220
5S	4	480	1920	4.27	8200
5T	5	510	3920	6.67	26200
5U	6	545	4110	20.74	85200

[a] Degree of methyl substitution on the benzene ring.

b. Benzene-d_6. The **4B**–TCNE system in DCM (Figure 4) yields a linear Scott graph (r = 0.979) at a C_D/C_T of 33:1 and a calculated saturation range of 4–8%. However, at a concentration ratio of 429:1, the Scott line is distinctly curved. This observation underscores another of Deranleau's cautions, i.e., "the smaller the range of saturation fraction being studied, the better will be the possibility that a straight line is obtained from either of these plots even if the entire experiment is represented by a highly curved line, which we note specifically is a general characteristic of equilibria involving other than 1:1 stoichiometry". In this instance the portion of the Scott graph covering the low saturation region appears to be reasonably linear because it covers a short segment of the entire curve and only neglible amounts of D_2T species are present at low saturation. At higher donor concentrations, the formation of D_2T species is forced, and the Scott graph appears strongly curved. Ho and Thompson[25] have calculated K values for both DT and D_2T complexes of benzene, toluene, and *p*-xylene in heptane and carbon tetrachloride.

Merrifield and Phillips[1] hypothesized and later investigators[2,4] confirmed that the absorbance band of **4A**–TCNE with λ_{max} 385 nm arises from transitions of electrons from the e_{1g} orbitals of **4A** to the π^* orbital of TCNE. The vertical IE of these orbitals from PES is 9.24 eV.[26] When this value is substituted into eq 1′, it yields a λ_{max} of 387 nm, which is in good agreement with the experimental value of 385 nm. Since the IE of **4B** is also 9.24 eV,[26] it is not surprising that the λ_{max} and band half-width values of **4B**–TCNE at 385–390 nm and 6000–6200 cm^{-1} are in close agreement with those of **4A**–TCNE, indicating that substitution of deuterium for hydrogen in benzene has little effect on the CT interaction with TCNE.

c. Summary and Conclusions. (1) The **4A**–TCNE system is linear over the saturation range 0–22%, indicating that D_2T species form in only negligible amounts.

(2) The **4B**–TCNE system is linear at saturation <8% but exhibits a distinct curvature at higher saturation, indicating that the formation of D_2T species is forced at high C_D/C_T values.

5. Alkyl- and Alkenylbenzenes. Accounts of the characteristics and analyses of the behavior of the TCNE complexes of benzene and 8 of 12 possible methylbenzenes are given in papers of Merrifield and Phillips[1] and Rossi et al.[4] Since these authors published neither C_D/C_T ratios nor saturation fraction ranges employed in their studies, we reinvestigated the eight recorded methylbenzene–TCNE complexes and characterized the four remaining complexes and several alkylbenzene–TCNE complexes as well, using the highest feasible C_D/C_T ratios and saturation fraction ranges. Our results generally agreed well with those of previous authors. A comprehensive summary of the alkylbenzene–TCNE complexes is given in Table I, and selected values for their characteristics are given in Table II. Some observations and generalizations about specific groups of these complexes follow.

Table III. Spectral Characteristics and Association Constants for Monoalkylbenzene–TCNE Complexes in Dichloromethane at 21 °C

code	% satn	λ_{max}, nm	ϵ, L/(mol cm)	K, L/mol	ϵK
5A	1–22	410	3890	0.19	740
5B	<1	410	1800	0.33	594
5C	2–5	410	2950	0.19	560
5D	3–7	413	3630	0.10	363
5E	1–3	415	8800	0.03	260

a. Monoalkylbenzenes. Merrifield and Phillips[1] and Rossi et al.[4] reported ϵ and K values for the **5A**–TCNE system of 3300 and 0.20 L/mol and 2680 and 0.26 L/mol. Our analysis of this system (Table I) yields a composite Scott graph (Figure 3) with good linearity (r = 0.988); we obtained ϵ and K values of 3890 and 0.19 L/mol over a saturation range of 1–22%.

Although each of three segments of the Scott graph for the **5B**–TCNE system appear to be linear, the set of segments does not fit on a straight line. In such a case it is reasonable to assume that the there are appreciable quantities of D_2T present and that the characteristics of the DT complex are most accurately represented by the segment covering the lowest saturation range. The results of a Foster–Matheson plot for the system at C_D/C_T = 1 are reported in Table I. Results obtained for systems at such low saturation levels have relatively poor reliability.

The K values of the monoalkyl–TCNE complexes (Table III) decrease progressively (n > iso > tert) with the bulk of the substituent alkyl showing the effect of steric hindrance between the donor and acceptor molecules. A study of *n*-alkylbenzene/TCNE systems (n = 1–5) in cyclohexane by Emslie et al.[27] showed that K values fell in the range 2.0–3.1 L/mol, indicating that chain length has little effect on steric hindrance. The relatively invariant values obtained for λ_{max} (405–415 nm) and $\Delta\nu_{1/2}$ (6500–6800 cm^{-1}) indicate that the CT energies of these complexes are only slightly affected by the bulkiness or length of the substituent alkyl group.

b. Dialkylbenzenes. The dimethylbenzene–TCNE systems yield linear Scott plots at saturation ranges of about 20–40%. Values of K for **5F**–, **5G**–, and **5H**–TCNE obtained by various authors range from 0.4 to 0.7 L/mol. The K value obtained for **5I**–TCNE (0.16 L/mol) reflects the additional steric hindrance of the ethyl group relative to methyl. The effective absorbance of the highly hindered **5J**–TCNE system is so small that meaningful results were not obtained. The evidence for D_2T species for **5H**–TCNE in heptane and CCl_4[25] as well as the curved Scott graphs we obtained for several alkylbenzene/TCNE systems indicates that D_2T species are also present in DCM solutions.

c. Trialkylbenzenes. Scott lines for the **5K** and the **5L**–TCNE systems are strongly curved at high C_D/C_T ratios; at low ratios these systems yield K values of 1.29 and 1.24 L/mol.

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[25] Ho, Y. E.; Thompson, C. C. *J. Chem. Soc., Chem. Commun.* **1973**, 609–610.

[26] Turner, D. W. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: London, 1970.

[27] Emslie, P. H.; Foster, R.; Horman, I.; Morris, J. W.; Twistelton, D. R. *J. Chem. Soc. B* **1969**, 1161–1165.

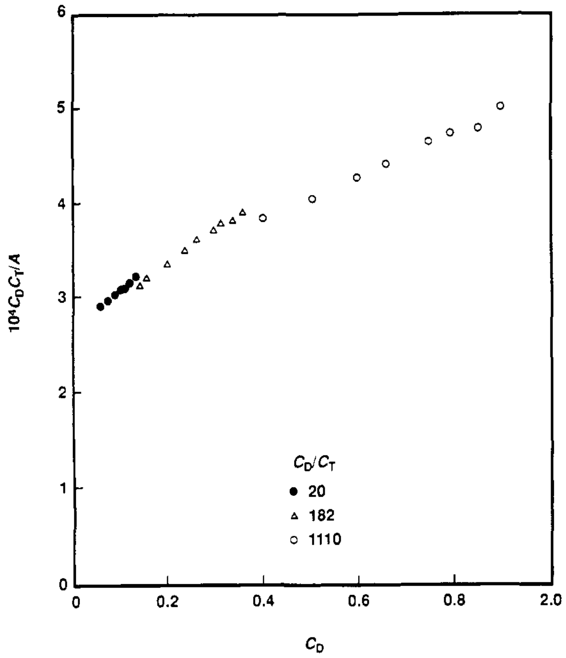

Figure 5. Scott graphs for mesitylene–TCNE systems.

The K values derived for 5N/TCNE systems at C_D/C_T = 20, 82, and 1110 increase progressively from 0.77 and 1.07 to 1.56. Although the Scott lines for each of the systems are straight over short ranges, the graph of the combined systems (Figure 5) shows distinct curvature, indicating that there is an abundance of D_2T species at high C_D/C_T ratios. The ϵ and K values reported by other authors fall squarely within the range of our values.

The relatively low value of K (0.27 L/mol) for 5O–TCNE is consistent with the high intermolecular steric hindrance expected for this system. The highly hindered 5O–TCNE system yields a strongly curved Scott line. However, the Foster–Matheson plot of 5M–TCNE with $C_D = C_T$ yields a surprisingly high K value of 1.70 L/mol.

d. Polyalkylbenzenes. Our values of ϵ and K for 5S–TCNE are in fair agreement with those of other authors even though they were determined from a system in which TCNE was in excess. Studies of the 5Q–TCNE system using C_D/C_T ratios of 1:20 and 19:1 yielded a straight Scott line in the first case and a curved Scott line in the second case. This provides further evidence that D_2T species are prevalent in alkylbenzene–TCNE systems, whereas DT_2 species are not.

No evidence for D_2T species is observed in the 5T and 5U–TCNE systems at saturation levels below 30%. Analysis of the 5V–TCNE system, however, yielded a Scott line with a negative slope, indicating that 5V–TCNE has an extremely small K value because of the steric interference of the six ethyl groups on the donor molecule. Castro et al.[28] used a similar steric argument to account for the weakness of the interaction between 5V and 1,3,5-trinitrobenzene. The structurally related hexamethyl complex 5U–TCNE by contrast, has one of the highest K values (20.74) ever reported for a hydrocarbon complex of TCNE.

e. Cyclopropylbenzene. The spectrum of the 5W–TCNE system in DCM (Figure 6) consists a of wide band with λ_{max} 405 nm and a strong shoulder sloping off at 450 nm. This band deconvolutes into two bands at 400 and 480 nm designated as λ_1 and λ_2. Shudo et al.[29] ascribes the first two ionizations at 8.61 and 9.12 eV in the PE spectrum of 5W to (1) a b_1-like orbital conjugated with the $e_a{}^*$ orbital of the cyclopropyl ring[30] and (2) an a_2-like orbital localized on the benzene ring. Shudo and Okamato[31] attributed λ_2 at 480 nm in the 5W–TCNE spectrum to a $\pi \rightarrow \pi^*$ transition from the b_1-like orbital. The PE ionizations at 8.61 and 9.12 eV, which correspond to CT transisions at 460 and 400 nm, support their assignment. A Scott analysis of 5W–TCNE indicates that it is a weak complex (K = 0.16 L/mol) and that it is the only complex present in appreciable amounts up to 18% saturation.

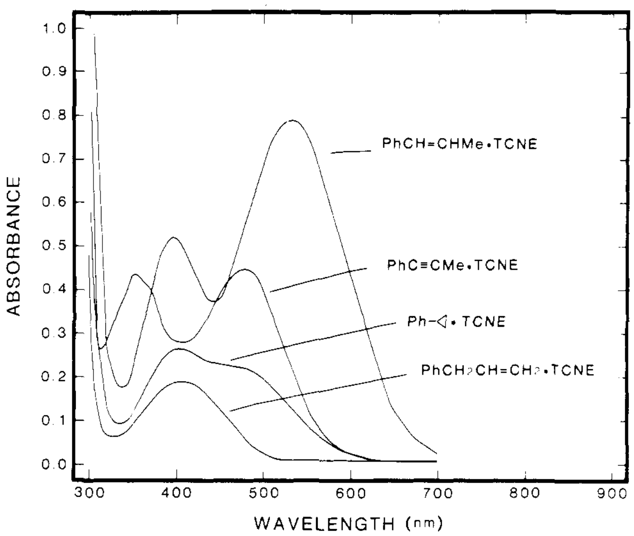

Figure 6. Spectra of phenylpropane–TCNE systems.

f. Allylbenzene. The spectrum of 5X–TCNE (Figure 6) with λ_{max} 405 nm and $\Delta\nu_{1/2}$ 7100 cm^{-1} is both blue-shifted and broader than the spectrum of 5C–TCNE with λ_{max} 415 nm and $\Delta\nu_{1/2}$ 6600 cm^{-1}. This difference is explained by assuming not only that TCNE undergoes at CT interaction with the a_2 and b_1 orbitals in 5X, as it does in the structurally related 5C molecule but also that TCNE interacts independently with the terminal double bond in 5X as well, giving rise to an additional weak absorbance at about 350 nm. This interpretation is supported by the observation that 2A–TCNE has a λ_{max} at 355 nm with about one-tenth the intensity of the CT bands of 5C–TCNE. Furthermore, Rabalais and Colton[32] reported PE ionizations for 5X at 8.85 (b_1), 9.27 (a_2), and 9.71 (π_e) eV, which correspond to CT transitions of 430, 385, and 345 nm for 5X–TCNE; these values agree well with the absorbances at 430, 395, and 355 nm and the orbital assignments proposed for 5X–TCNE.

g. Summary and Conclusions. The generalizations drawn from the discussion of methylbenzenes in this section can be assumed to apply to alkylbenzenes in which there are no pronounced steric or structural effects. Table II contains selected estimates of λ_{max}, ϵ, and K for the methylbenzene–TCNE complexes. These data have been used to validate the parameters of eq 7–9 below. Values that appear in parentheses in Table II have been calculated by using eq 8.

(1) The absorbance spectra of TCNE complexes of the alkylbenzenes appear as single broad bands with the ex-

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[28] Castro, C. E.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 2322–2326.

[29] Shudo, K.; Kobayashi, T.; Utsunomiya, C. *Tetrahedron* **1977**, *33*, 1721–1724.

[30] Prins, I.; Verhoeven, J. W.; deBoer, Th. J.; Worrell, C. *Tetrahedron* **1977**, *33*, 127–131.

[31] Shudo, K.; Okamoto, T. *Tetrahedron* **1977**, *33*, 1717–1719.

[32] Rabalais, J. W.; Colton, R. J. *J. Electron Spectrosc.* **1972/73**, *1*, 83–99.

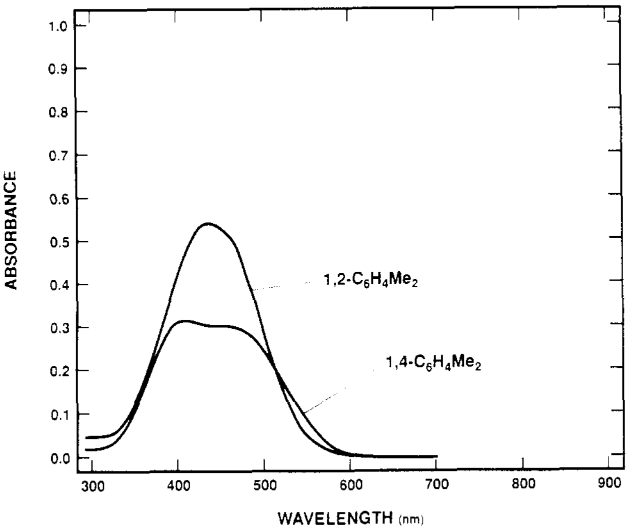
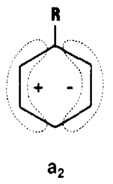
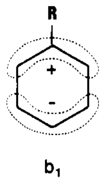


Figure 7. Spectra of dimethylbenzene–TCNE complexes.

ception of the *p*-dialkyls **5H**–, **5I**–, and **5J**–TCNE, each of which has two distinct maxima (Figure 7). The single bands are composites of two strongly overlapping bands, λ_1 and λ_2, which arise from electronic transitions between the a_2 and b_1 orbitals of the benzenoid ring (structures IV and V) and the π^* orbital of TCNE. The a_2 and b_1 orbitals in **4A**, **5N**, and **5U** are degenerate; consequently λ_1 and λ_2 for the TCNE complexes of these donors are identical and their bands are relatively narrow. In all the other methylbenzenes, except **5G**, the energy of the b_1 orbitals is higher than that of the a_2 orbital.



IV



V

(2) Given that an electron-releasing methyl reference substituent R_1 is attached to a benzenoid ring at position 1 corresponding to the node of the a_2 orbital (structure IV) and the antinode of the b_1 orbital (structure V), it is inferred from the analysis of the PE spectra that a methyl group R_4, para to R_1, elevates the energy of b_1 relative to a_2. E.g, the IE values of a_2 and b_1 in **5A** are 9.00 and 8.78 eV,[33] a difference of 0.22 eV; the corresponding IE values in **5H** are 9.14 and 8.43 eV,[34] a difference of 0.71 eV. In **5A**, the methyl group, by virtue of its location at the antinode of the b_1 orbital and at the node of the a_2 orbital, elevates the energy of the b_1 orbital 0.22 eV relative to the a_2 orbital. In **5H**, the *p*-methyl groups act in concert to elevate the energy of the b_1 orbital by 0.71 eV relative to the a_2 orbital.

Corresponding differences are observed in the spectra of **4A**–, **5A**–, and **5H**–TCNE. The value of λ_{max} in **4A**–TCNE is 385 nm. The λ_1 and λ_2 values obtained by the deconvolution of the spectrum of **5A**–TCNE are 395 and 425 nm, whereas the λ_1 and λ_2 values for **5H**–TCNE are about 390 and 465 nm. While the methyl substituents in these complexes have scarcely any effect on the values of λ_1, both the first methyl and the second *p*-methyl increase λ_2 by about 40 nm each.

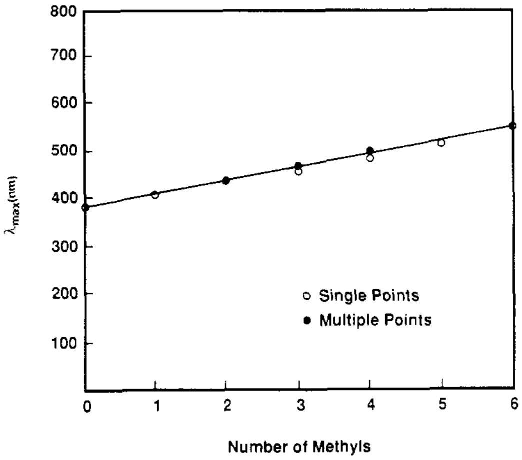


Figure 8. λ_{max} vs number of methyls for methylbenzene–TCNE complexes.

(3) Methyl substituents ortho or meta to R_1 are expected to have a relatively smaller effect on the energy differences between a_2 and b_1 orbitals because such substituents interact moderately well with both types of orbitals. The IE values for the a_2 and b_1 orbitals for **5F** are 8.90 and 8.45 eV,[32] giving a difference of 0.45 eV; the corresponding values for **5G** are 9.03 and 8.55 eV,[33] giving a nearly identical difference of 0.48 eV. This shows that an *o*- or *m*-methyl substituent is about 65% as effective as a *p*-methyl in splitting the energies of a_2 and b_1 orbitals.

Since the spectra of **5F**– and **5G**–TCNE are virtually identical, it is assumed that the values of λ_1 and λ_2 (about 420 and 455 nm), obtained by deconvoluting the spectrum of **5F**–TCNE,[4] are also the same. We note that both λ_1 and λ_2 are elevated 25–30 nm above their corresponding values in **5A**–TCNE, as expected from the previous consideration of the IE values of **5A**, **5F**, and **5G**. In summary: (a) the *o*- and *m*-methyl substituents effect increases of 25–30 nm in both λ_1 and λ_2 of methylbenzene–TCNE complexes; (b) the *p*-methyl substituent effects an increase of 40 nm in values of λ_2 alone for methylbenzene–TCNE complexes.

(4) Examination of the λ_{max} values of alkylbenzene–TCNE complexes in Table II shows that λ_{max} values tend to increase as the number of substituents on the benzenoid ring increases. The plot of λ_{max} of the methylbenzene–TCNE complexes versus the number of methyls, n, attached to the benzene ring (Figure 8) yields a straight line with the equation

$$\lambda_{max} = \lambda_0 + Bn = 382 + 26.7n \qquad (7)$$

Here λ_0 is the extrapolated value of λ_{max} for **4A**–TCNE (experimental value = 385 nm) and B is the mean increase in λ_{max} per additional methyl. The correlation coefficient for eq 7 is 0.994. We note that λ_{max} is a characteristic of a composite band and is approximately equal to the average of λ_1 and λ_2. The value of λ_{max} selected for **5H**–TCNE is the average of the two maxima at 415 and 460 nm observed in its spectrum.

(5) The K values for the methylbenzene–TCNE complexes taken from Table II also increase with the degree of substitution n. A plot of log K versus n yields a straight line (Figure 9) described by the equation

$$\log K = \log K_0 + Bn = -1.04 + 0.40n \qquad (8)$$

where K_0 represents the association constant of **4A**–TCNE. The correlation coefficient is 0.994. The calculated value

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(33) Heilbronner, E.; Maier, J. P. *Electron Spectroscopy: Theory, Techniques and Applications*; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977; p 245, footnote 74.

(34) Koenig, T.; Tuttle, M.; Weilesek, R. A. *Tetrahedron Lett.* **1974**, 2537–2540.

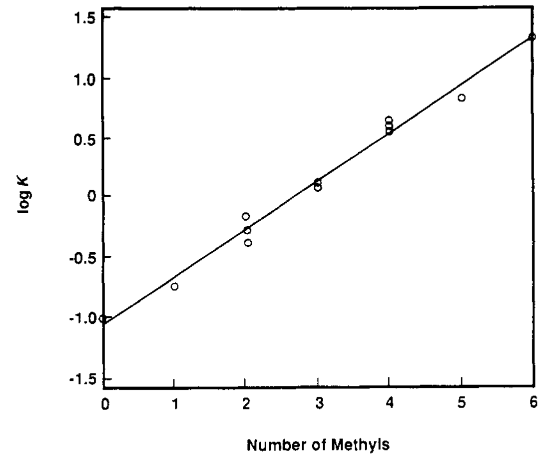

Figure 9. log K vs number of methyls for methylbenzene–TCNE complexes.

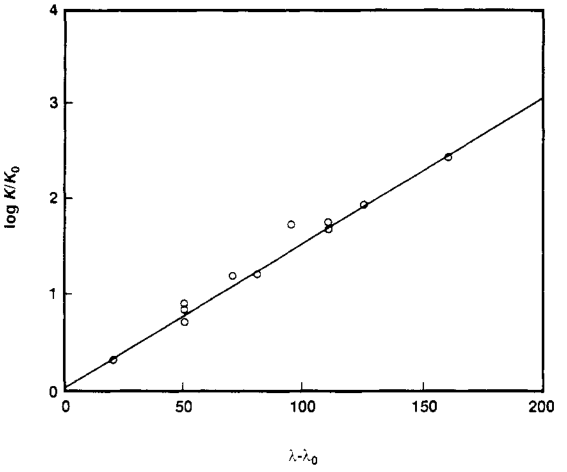

Figure 10. log K vs $\lambda - \lambda_0$ for methylbenzene–TCNE complexes.

of K_0 (0.090 L/mol) is close to the experimental values reported in the literature (0.10[1] and 0.11[4] L/mol); the calculated value of K for **5A**–TCNE (0.225 L/mol) also agrees closely with the reported experimental values (0.20[1] and 0.26[4] L/mol).

(6) It follows that if both λ_{max} and log K are linearly related to n, there must also be a simple relationship between λ_{max} and log K. Such a relation was derived by Dewar and Thompson[35] and expressed in the form

$$\log (K/K_0) = C(\lambda_{max} - \lambda_0) = 0.013(\lambda_{max} - 385) \quad (9)$$

The λ_0 and K_0 values for **4A**-TCNE are taken from Table II. The correlation coefficient is 0.992. The favorable fit of the data (Figure 10) indicates a close relationship between the CT energy and thermodynamic stability of the complexes and suggests that the stabilities of these complexes are due primarily to CT interactions.

(7) Replacement of a methyl by a higher alkyl generally produces only a slight effect on λ_{max} of an alkylbenzene–TCNE complex as shown by a comparison of **5A**–, **5H**–, **5L**–, **5O**–, and **5U**–TCNE with each of their alkyl congeners. However, K values tend to decrease with the bulk or steric hindrance of the substituent alkyl group. The complexes of all *tert*-butylbenzenes with TCNE are CCT complexes because the bulky *tert*-butyl group is very effective in hindering the close overlap between the donor and acceptor orbitals.

(8) Many of the alkylbenzene–TCNE systems studied to date show evidence for the presence of D_2T species at high C_D/C_T ratios; however, no evidence has been found for DT_2 species.

6. Alkyldibenzenes, Biphenyls, and Bridged Biphenyls. This section covers complexes in which the donor molecule contains two benzenoid rings wherein the rings are (a) conjoined by a methylene and/or an imino group or (b) joined directly together.

a. Alkyldibenzenes. Scott analyses of the **6A**–TCNE system at C_D/C_T ratios of 10:1 and 58:1 yield different values of ϵ and K, indicating the presence of D_2T species. This system has a spectrum nearly identical with that of the **5A**–TCNE (K = 0.19 L/mol) but has a larger K value (1.20 L/mol) as expected when the donor molecule has two independent benzene rings. Similarly the spectra of **6B**– and **5V**–TCNE are alike in all respects although the K value for **6B**–TCNE (0.50 L/mol) is much larger than that of **5V**–TCNE (0.16 L/mol).

The spectra of the ortho-disubstituted complexes **6C**–TCNE (λ_{max} 435 nm, $\Delta\nu_{1/2}$ 6800 cm^{-1}) and **5F**–TCNE (λ_{max} 435 nm, $\Delta\nu_{1/2}$ 6400 cm^{-1}) are similar except for an appreciable red-shifted broadening observed in **6C**–TCNE. This broadening is evidence of a slight through-space interaction between the orbitals of the rings which are tilted toward each other at a dihedral angle of about 120°. Kobayashi et al.[36] rationalized the PE spectrum of the structurally related triptycene molecule in terms of a through-space interaction between the b_1-like orbitals of its benzene rings. The K value for **6C**–TCNE (1.09 L/mol) is nearly double that of **5F**–TCNE (0.67 L/mol) as expected for a complex with twice as many equivalent binding sites. The characteristics of **6D**–TCNE are presented to show the effect of replacing a methylene in **6C** with an imino group. The nonbonded electrons of the imino nitrogen elevate the energy of the b_1-like orbitals, leading to a high value of λ_2 (810 nm), and increase the basicity of the donor orbitals, leading to a value of K (2.78 L/mol).

Cram and Bauer[37] reported that the λ_{max} values of a series of paracyclophane–TCNE complexes increase as the rings in the donor molecule are forced more closely together. We determined that one of these complexes, **6E**–TCNE (λ_{max} 515 nm), had ϵ and K values of 2210 and 2.60 L/mol, which are significantly different from those of the *p*-dimethyl complex **5H**–TCNE (λ_1 415, λ_2 460 nm), with ϵ and K values of 2880 and 0.45 L/mol. The single narrow absorbance band of **6E**–TCNE indicates that the energies of both the a_2- and b_1-like orbitals of **6E** are elevated equally by the strong compression of the π orbitals between the rings. This interpretation is supported by an analysis of the PE spectrum of **6E** reported by Kovac et al.[38] The high K value of **6E**–TCNE indicates that the donor ability of the π orbitals of **6E** is greatly enhanced by their compression.

b. Biphenyls and Bridged Biphenyls. The ϵ and K values derived for the **6F**–TCNE system vary significantly with the concentration ratio of the stock solutions, indicating the presence of appreciable amounts of D_2T species. The spectrum of **6F**–TCNE (Figure 16), unlike that of **4A**–TCNE, consists of two bands (λ_1 390, λ_2 495 nm). The first band arises from a transition originating in the a_2-like orbital which is unaffected by inter-ring interactions, whereas the second band arises from an extended π orbital

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[35] Dewar, M. J. S.; Thompson, C. C. *Tetrahedron Supple.* **1966**, *7*, 97–114.

[36] Kobayashi, T.; Kubota, T.; Ezumi, K. *J. Am. Chem. Soc.* **1983**, *105*, 2172–2174.

[37] Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977.

[38] Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314–4324.

which results from the combination of the b_1-like orbitals. This interpretation is supported by the PE studies of Ruscic et al.[39]

The absorbance bands of the **6G**–TCNE (λ_1 415, λ_2 565 nm) are red-shifted relative to **6F**–TCNE (λ_1 390, λ_2 495 nm). The 25-nm shift in λ_1 is due to the inductive interaction of the methylene with the a_2-like orbital of **6G**. The 70-nm shift in λ_2 is partly due to the inductive interaction of the methylene with the b_1-like orbital. It is primarily due, however, to the low IE of the delocalized π orbital arising from the inter-ring conjugation of the b_1-like orbitals which are held in the optimal coplanar configuration by the bridging methylene. Suzuki[40] estimated an interplanar angle of 20° for **6F** in solution from studies of UV spectra. Since this angle is far from that required for optimal conjugation, the value of λ_2 for **6F** is much smaller than for **6G**.

The fact that the spectrum of **6H**–TCNE (λ_1 425, λ_2 560 nm) is strikingly similar to that of **6G**–TCNE indicates that the two rings in **6H** are nearly coplanar in solution. This interpretation is supported by Suzuki,[41] who arrived at the same conclusion through the study of UV spectrum of **6H**.

Characteristics of **6I**–TCNE[6] are included because of its structural resemblance to **6G**–TCNE. We note that λ_2 (600 nm) and K (1.46 L/mol) are larger than the corresponding values for **6G**–TCNE, reflecting the strong conjugation between the nonbonded electron pair of the imino nitrogens and the b_1-like orbitals of the benzene rings.

c. Summary and Conclusions. (1) The K values of TCNE complexes with donor molecules containing two unhindered benzenoid rings are significantly larger than those of structurally related complexes having only one ring, indicating that stability tends to increase with the availability of bonding sites.

(2) For TCNE complexes of donor molecules in which the electrons of two benzenoid rings are squeezed together, λ_1, λ_2, and K values tend to increase as the compression is increased.

(3) For TCNE complexes of biphenyl and its bridged derivatives, λ_2 tends to increase as the dihedral angle between the two rings approaches 0°, the configuration of optimum conjugation between the b_1-like orbitals.

7. Styrenes. In the following discussion **7A** and its derivatives are treated as molecules in which a vinyl group is attached to a benzene ring at a point where the a_2 orbital has a node and the b_1 orbital has an antinode. Conjugation between the ethylenic π orbital (π_e) and the b_1 orbital is assumed to be optimal when the interplanar angle between the ethenyl carbons and the benzene ring is 0°. Steric factors that hinder the attainment of coplanarity also inhibit conjugation and prevent the conjugated orbital system from reaching its optimal potential energy.

a. Styrene. Scott analysis of the **7A**–TCNE system (Figure 11) using C_D/C_T ratios of 15:1 and 76:1 yield distinctly different values for ϵ and K, indicating the presence of significant amounts of D_2T species in solution. The spectrum of **7A**–TCNE consists of two bands at λ_1 395 and λ_2 480 nm. The first band is due to an $a_2 \rightarrow \pi^*$ transition between **7A** and TCNE; the second band arises from the MO formed by the combination of the π_e and b_1 orbitals. This interpretation is supported by an analysis of the PE spectrum of **4A** by Rabalais and Colton,[32] who assigned the ionization bands at 8.48 and 9.28 eV to the b_1- and a_2-like orbitals. Substitution of these IE values into eq 1′ yields CT energies equivalent to 479 and 383 nm, which are close to the experimental values for **4A**–TCNE. Since PES studies of Maier and Turner[42] indicate that the interplanar angle in **7A** is 0°, λ_2 480 nm will serve as the value corresponding to optimal unhindered and unstrained π_e–b_1 conjugation in the styrene moiety of TCNE complexes.

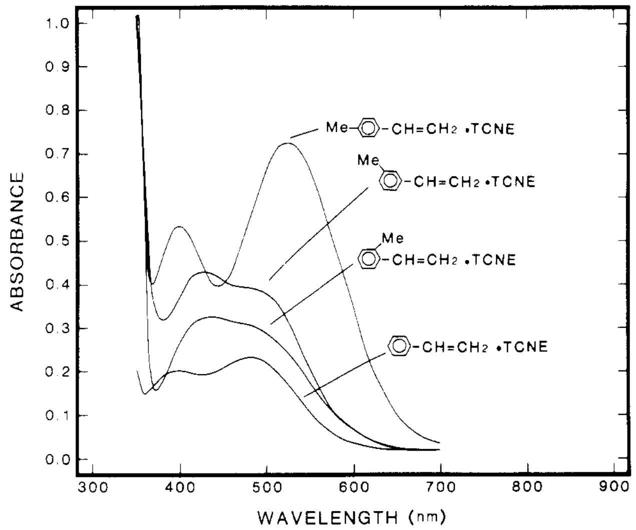

Figure 11. Spectra of monomethylstyrene–TCNE complexes.

b. Ring-Substituted Methylstyrenes. In the study of the TCNE complexes of these styrene derivatives, it is useful to compare them to their structural analogues among the methylbenzenes. In this sense the monomethylstyrenes **7B**, **7C**, and **7D** are similar to the dimethylbenzenes **5F**, **5G**, and **5H** in which a methyl is replaced with a vinyl group; the dimethylstyrenes **7E** and **7F** are analogous to **5L**, and **7G** is analogous to **5K**; the tri- and pentamethylstyrenes **7H** and **7I** are analogous to **5Q** and **5T**.

i. Monomethylstyrenes. Of the three monomethylstyrene–TCNE systems only **7B**- and **7D**–TCNE yield definitive values of ϵ and K over a large saturation range. The **7B**–TCNE system apparently contains significant amounts of D_2T species. Comparison of the values of the ϵK product of **7B**- and **7D**–TCNE (710 and 900) with those of the **5F**-, **5G**-, and **5H**–TCNE (2170, 1730, and 1300) indicates that these styrenes have a lower effective absorbance than their methylbenzene analogues. However, the styrene complexes have much larger K values (2.82 and 2.66 L/mol) than the corresponding methylbenzene complexes (0.55, 0.57, and 0.45 L/mol). This indicates that the vinyl group is more effective than methyl in releasing electrons to the benzene ring through its ability to conjugate with the b_1 orbital.

The above inference is borne out by a study of the absorbance spectra of the complexes (Figure 11). The λ_1 values of **7B**-, **7C**-, and **7D**–TCNE (425, 425, and 395 nm) are nearly identical with those determined for **5F**-, **5G**-, and **5H**–TCNE (420, 420, and 390 nm), indicating that λ_1 for the monomethylstyrene–TCNE complexes arises from an $a_2 \rightarrow \pi^*$ transition. It can also be inferred that the *o*- and *m*-methyl groups in **7B** and **7C** donate electrons to the a_2 orbitals through induction and/or hyperconjugation, whereas the *p*-methyl group in **7D** does not.

The λ_2 values of **7B**-, **7C**-, and **7D**–TCNE (495, 505, and 525 nm) are somewhat higher than that of **7A**–TCNE at

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[39] Ruscic, B.; Kovac, B.; Klasinc, L.; Güsten, H. *Z. Naturforsch.* **1978**, *33a*, 1006–1012.

[40] Suzuki, H. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1340–1350.

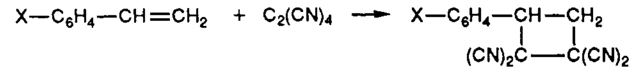
[41] Suzuki, H. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1357–1361.

[42] Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196–206.

480 nm, indicating that the *o*-, *m*-, and *p*-methyls all donate electrons to the b_1 orbitals but that their effectiveness increases in the order ortho < meta < para. Apparently the hyperconjugative–inductive contribution of the *o*-methyl to the b_1 orbital is partially offset by its steric inhibition of π_e–b_1 conjugation between the benzene ring and vinyl group. PES studies of **7B** yield a value of 22° for the interplanar angle.[40] The particular effectiveness of the *p*-methyl in donating electrons to the b_1 orbitals is due to its location at the antinode of the orbital opposite the vinyl group.

The rules regarding the effect of methyl substitution on λ_1 and λ_2 of the methylbenzene–TCNE complexes (see section 5g) apply to the monomethylstyrene–TCNE complexes with one exception. The sole difference is that an *o*-methyl, by strongly hindering the movement of the adjacent ethenyl group, has an inhibiting effect on the π_e–b_1 conjugation.

ii. Dimethylstyrenes. Of the three dimethylstyrene–TCNE systems studied, **7F**- and **7G**–TCNE form stable solutions, whereas **7E**–TCNE does not. A mixture of **7E** and TCNE in DCM is rose colored; however, the color fades irreversibly within several minutes. Although no attempts were made to determine the nature of the reaction, it is believed that **7E** and TCNE form a complex that precedes a 1,2-cycloaddition reaction of the type which was



$$X{-}C_6H_4{-}CH{=}CH_2 + C_2(CN)_4 \longrightarrow X{-}C_6H_4{-}\underset{(CN)_2C}{CH}{-}\underset{C(CN)_2}{CH_2}$$

reported by Williams et al.[43] Here X is an electron-donating group. Evidence for the presence of **7E**–TCNE in the freshly mixed solution comes from the fact that the two absorbance maxima at 435 and 525 nm are close to the values expected for a complex of TCNE with a styrene containing both an *o*- and a *p*-methyl group. The electron-donating effect of the *o*-methyl on the b_1 orbitals of **7E** is apparently offset by steric inhibition of the π_e–b_1 conjugation; otherwise λ_2 would be expected to have a value of about 550 nm.

The spectrum of **7F**–TCNE consists of a broad band with λ_{max} 475 nm and $\Delta\nu_{1/2}$ 7300 cm^{-1}, which resolves into bands λ_1 460 and λ_2 540 nm. We note here the effect of an *o*- and a *m*-methyl on the value of λ_1, which is about 35 nm larger than the corresponding value in **7B**–TCNE.

The spectrum of **7G**–TCNE consists of a band with λ_{max} 465 nm and $\Delta\nu_{1/2}$ 5700 cm^{-1}, which strongly resembles that of **5K**–TCNE with λ_{max} 465 nm and $\Delta\nu_{1/2}$ 5800 cm^{-1}. These similarities are taken as evidence that the rotation of the vinyl group about the C–C axis in **7G** is so severely restricted by the two *o*-methyls that it represses the π_e–b_1 conjugation to the extent that the effect of the vinyl group on the energy of the b_1 orbital is no greater than that of an alkyl group. Furthermore the *K* value of **7G**–TCNE (1.15 L/mol) is smaller than that of **5K**–TCNE (1.29 L/mol), indicating that the vinyl group, by projecting out of the plane of the ring, may hinder complex formation. This interpretation is supported by the results of the PES study of Maier and Turner,[42] who estimated that the interplanar angle in **7G** is as high as 55°. Their ionization energy values of 8.65 and 8.45 eV, when substituted into eq 1′, yield λ_1 and λ_2 values of 455 and 484 nm for **7G**–TCNE, which are close to the values (455 and 480 nm) estimated by deconvolution of the 465-nm band.

iii. Polymethylstyrenes. The spectrum of **7H**–TCNE consists of a band with λ_{max} 480 nm and $\Delta\nu_{1/2}$ 6500 cm^{-1}, which is strongly skewed toward the red. Visual comparison of the spectra of **7G**- and **7H**–TCNE shows that the λ_2 value of the latter is about 30 nm larger than the former. These comparisons indicate that the *p*-methyl group in **7H** interacts primarily with the b_1 orbital and has no appreciable effect on the energy of the a_2 orbital.

The spectral characteristics of **7I**–TCNE (λ_{max} 540 nm, $\Delta\nu_{1/2}$ 5300 cm^{-1}) are almost indistinguishable from those of **5U**–TCNE (λ_{max} 540 nm, $\Delta\nu_{1/2}$ 5400 cm^{-1}). This indicates that the a_2 and b_1 orbitals in **7I** are essentially degenerate as they are in **5U** and that the severely restricted vinyl group, being rotated out of the plane of the ring and unable to conjugate with the ring orbitals, has about as much influence on the energy of the b_1 orbital as an alkyl group. It is also of interest to note that the *K* values of **7H**- and **7I**–TCNE (2.33 and 5.31 L/mol) are significantly smaller than the *K* values of their methylbenzene analogues **5R**- and **5U**–TCNE (3.81 and 20.74 L/mol). This is further evidence that the projecting vinyl group may hinder the contact between the donor and TCNE molecules. The large value of λ_{max} for **7I**–TCNE (540 nm) relative to **7H**–TCNE (480 nm) indicates that the two extra *m*-methyls in **7I** interact with both the a_2 and b_1 orbitals.

iv. Summary and Conclusions. As noted before, the spectrum of **4A**–TCNE consists of a single narrow band at 385 nm arising from transitions from the degenerate a_2 and b_1 orbitals, whereas the spectrum of **7A**–TCNE consists of two distinct bands at 395 and 480 nm. The π_e–b_1 conjugation between the vinyl substituent and the benzene ring in **7A** removes the degeneracy and has the effect of increasing λ_2 by 95 nm with respect to **4A**–TCNE while having virtually no effect on λ_1. The substitution of one or more methyl groups on **7A** may increase both λ_1 and λ_2 by 0–75 nm per methyl relative to **7A**–TCNE depending upon the location of the methyl group on the ring. The following generalizations regarding the effect of methyl substitution on λ_1 and λ_2 are based on the assumption that the vinyl group in styrene and its methyl derivatives is always coincident with the node of the a_2-like orbital and with the antinode of the b_1-like orbital.

(1) The substitution of a methyl para to an unhindered vinyl group increases λ_2 of the TCNE complex by 50 nm but has no appreciable effect on λ_1, showing that a *p*-methyl interacts only with the b_1 orbital.

(2) The substitution of a methyl group meta to the vinyl group increases λ_1 and λ_2 of the TCNE complex by 45 and 15 nm per methyl, indicating that a *m*-methyl donates electrons more effectively to the a_2 orbital.

(3) Substitution of methyl groups ortho to the vinyl group increases λ_1 of the TCNE complex by 30 nm per methyl, indicating that *o*-methyls donate electrons to the a_2 orbital.

However, substitution of a single methyl ortho to a vinyl group leads to an increase of only 5–15 nm in λ_2 of the TCNE complex because the π_e–b_1 conjugation is partially inhibited by the steric hindrance of the methyl group itself which prevents the vinyl group from attaining the coplanar configuration required for optimum conjugation.

Substitution of two methyls ortho to a vinyl group causes such severe steric hindrance that it leads to complete inhibition of π_e–b_1 conjugation. Consequently, the electron-releasing ability of the vinyl group is completely nullified, and the vinyl group has no more effect on changing λ_2 than an alkyl group.

(4) While there is no simple relationship between the degree of methyl substitution, *n*, and log *K* or λ_{max} as there is for the methylbenzene–TCNE complexes, the product ϵK is seen to increase uniformly with *n*. It is noteworthy

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[43] Williams, J. K.; Wiley, D. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1962**, *84*, 2210–2215.

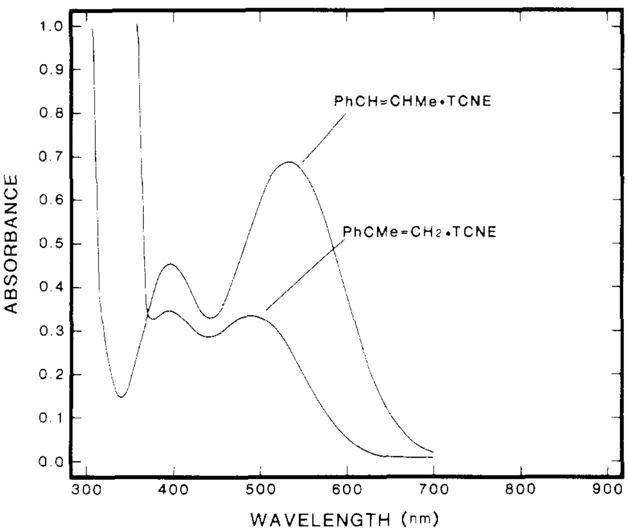

Figure 12. Spectra of α,β-methylstyrene–TCNE complexes.

that K values of TCNE complexes of ring-substituted methylstyrenes are larger than K values of cognate methylbenzene–TCNE complexes that have the same total number of substituents on the benzene ring, except in those cases where the styrene has two *o*-methyls. This suggests that a vinyl group that is constricted by two *o*-methyls projects so far out of the plane of the benzene ring that it hinders the interaction of TCNE with the donor orbitals. The lack of correlation between n and log K may be due to such a steric factor.

c. Chain-Substituted Methylstyrenes. This section deals with TCNE complexes of methylstyrenes in which the methyls are substituted exclusively on the vinyl group. The compound 1-phenyl-1-cyclohexene, **7L**, is included in this section because of its close structural similarity to α,β-dimethylstyrene.

i. α- and *trans*-β-Methylstyrene. The spectra of **7J**– and **7K**–TCNE (Figure 12) are similar to that of **7A**–TCNE. In all three cases, λ_1 values are nearly identical at 395–400 nm, indicating that these bands arise from $a_2 \rightarrow \pi^*$ transitions which are unaffected by the methyl substituents on the ethenyl group. However the λ_2 values for **7A**–, **7J**–, and **7K**–TCNE are 480, 495, and 530 nm, which indicates that the energy of the b_1 orbital is sensitive to the location of the methyl groups.

In section 2 it was noted that λ_{max} for alkene–TCNE complexes increased by 60–65 nm per alkyl substituent on the ethenyl moiety. If this pattern were followed by the chain-substituted methylstyrenes, we would expect to observe λ_2 values of 540–545 nm for both **7J**– and **7K**–TCNE. In this respect the value of λ_2 for **7L**–TCNE (530 nm) has the expected value, and we can infer that the *trans*-β-methyl group in **7K** is donating electrons to the π_e–b_1 orbital. The relatively low value of λ_2 for **7J**–TCNE (495 nm) suggests that π_e–b_1 conjugation is inhibited by steric interference between the α-methyl group and the *o*-hydrogens on the benzene ring. This conjecture is supported by the PES studies of Maier and Turner,[42] which yield values of 38° and 0° for the interplanar angles in **7J** and **7K**.

ii. 1-Phenyl-1-cyclohexene and β,β-Dimethylstyrene. These compounds are juxtaposed because they permit a comparison of the relative steric effects of the α-methyl and the *cis*-β-methyl groups on π_e–b_1 conjugation. The spectrum of **7L**–TCNE consists of two bands at λ_1 400 and λ_2 560 nm. The first band is due to an $a_2 \rightarrow \pi^*$ transition. The second band is 70 nm larger than λ_2 for **7J**–TCNE (490 nm) as expected. The λ_2 band for **7M**–TCNE (545 nm) is 15 nm smaller than λ_2 for **7L**–TCNE. This suggests that *cis*-β-methyl of **7M** interacts sterically with the *o*-hydrogens of its benzene ring to inhibit π_e–b_1 conjugation. Support for this interpretation comes from the UV studies of Suzuki,[44] who estimated an interplanar angle of 40° for **7M** which was attributed to steric factors.

iii. Summary and Conclusions. Analysis of the spectra of **7J**–, **7K**–, **7L**–, and **7M**–TCNE leads to the following generalizations concerning the chain-substituted methylstyrenes.

(1) Methyls substituted on the ethene group of a styrene have no effect on λ_1, indicating that they do not release electrons to the a_2 orbital.

(2) A *trans*-β-methyl increases λ_2 by 50 nm relative to λ_2 in **7A**–TCNE, indicating that it donates electrons to the π_e–b_1 orbital of the styrene derivative.

(3) The substitution of an α- or *cis*-β-methyl on the vinyl group results in an increase in λ_2 of only 15–30 nm relative to λ_2 in **7A**–TCNE because the steric interaction between the methyl and the *o*-hydrogens inhibits π_e–b_1 conjugation.

d. Ring- and Chain-Substituted Alkylstyrenes. This section deals with TCNE complexes of styrene derivatives that have alkyl or alkenyl substitution on both the benzene ring and the vinyl group.

i. Indene and 1,2-Dihydronaphthalene. The vinyl group in each of the compounds **7N** and **7O** is part of a cyclic system attached to ortho positions on a benzene ring which fixes the angle between the ethenyl group and the benzene ring. In **7N** the methylene group serves a dual function as both an *o*- and a *cis*-β-substituent. In addition it locks the double bond and benzene ring into the coplanar conformation required for optimal conjugation. The spectrum of **7N**–TCNE has λ_1 and λ_2 bands at 420 and 540 nm, which indicates that the methylene group donates electrons to both the a_2 orbital of the benzene ring and to the conjugated π_e–b_1 MO. This conclusion is supported by the orbital assignments of PE ionizations of **7N** by Güsten et al.;[45] their IE values of 8.93 and 8.14 eV correspond to λ_1 and λ_2 values of 420 and 536 nm for **7N**–TCNE, which are close to the experimental values.

In **7O** two conjoined methylenes bridge the ortho position on the benzene ring and the cis-β position of the vinyl group. The spectrum of **7O**–TCNE has λ_1 and λ_2 bands at 425 and 565 nm. This indicates that the two methylenes serve the same function as the methylene in **7N** and that the π_e–b_1 conjugation is nearly optimal. The K values of **7N**– and **7O**–TCNE are practically identical, reflecting the great similarity between the two donors.

ii. Diisopropenylbenzenes. The spectra of **7P**– and **7Q**–TCNE can be best understood in reference to the spectrum of **7J**–TCNE when **7J** is regarded as a monoisopropenyl derivative of benzene. The spectrum of **7J**–TCNE consists of two bands at 400 and 490 nm, the first of which is due to an $a_2 \rightarrow \pi^*$ transition, and the second due to a transition from the b_1-like orbital. The compound **7Q** contains two *p*-isopropenyl groups, which are expected to conjugate cooperatively and exclusively with the b_1 orbital. Consequently **7Q**–TCNE should exhibit a band at about 400 nm and a second narrow band at about 580 nm. The actual spectrum of **7Q**–TCNE consists of a weak shoulder at 410 nm and a stronger symmetrical band at 575 nm with $\Delta\nu_{1/2}$ 5000 cm^{-1}.

The compound **7P** contains two *m*-isopropenyl groups, one of which is expected to conjugate strongly with the b_1 orbital and the other to conjugate less strongly with the

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[44] Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 619–628.

[45] Güsten, H.; Klasinc, L.; Ruscic, B. *Z. Naturforsch.* **1976**, *31a*, 1051–1056.

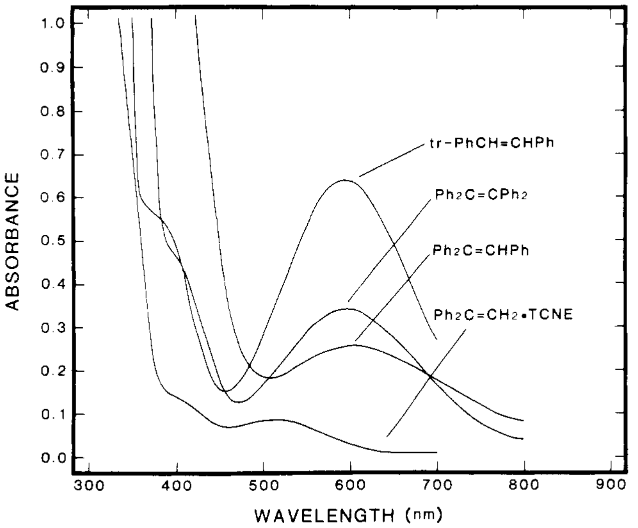

Figure 13. Spectra of polyphenylethylene–TCNE complexes.

a_2 orbital. Consequently the spectrum of **7P**–TCNE should consist of two bands in the vicinity of 500 nm. The actual spectrum of **7P**–TCNE exhibits a broad ($\Delta\nu_{1/2}$ 6800 cm^{-1}) symmetrical band at 505 nm. The width and shape of this band indicate that it is a composite of two bands, λ_1 and λ_2, at about 480 and 530 nm, which are attributed to transitions from the a_2- and b_1-like orbitals.

The K value of **7P**–TCNE (1.70–2.35 L/mol) is seen to increase with the degree of saturation; however, it is in the normal range for a methylstyrene–TCNE complex. The K value for **7Q**–TCNE (7.26 L/mol) is unusually large, indicating that the b_1-like orbital in **7Q** is a strong electron donor.

iii. Summary and Conclusions. (1) A vinylic group locked into a coplanar conformation on a benzene ring conjugates optimally with the b_1 orbital of the ring.

(2) In molecules such as indene, which contains a vinylic side chain attached at both ends to ortho positions on a benzene ring, the double bond conjugates with the b_1 orbital of the benzene ring and the alkyl end of the side chain interacts with the a_2 orbital of the benzene ring.

(3) Vinylic side chains para to one another conjugate cooperatively with the b_1 orbital of the benzene ring to which they are mutually attached. Vinylic groups meta to one another conjugate with both the a_2 and b_1 orbitals.

8. Polyphenylalkenes. Ethylene derivatives with two or more phenyls attached to the double-bonded carbons are considered in this section.

a. Diphenylethylenes. Laarhoven and Nivard[46] first reported the characteristics of **8B**– and **8C**–TCNE. However, we obtained definitive values of ϵ and K over an extended saturation range for **8C**–TCNE alone, and even in this case we were unable to reproduce the published values. Scott analyses of the **8A**– and **8C**–TCNE systems indicate that significant amounts for the D_2T species are present. However, ϵ and K values for **8B**–TCNE (2350–2620 and 0.18 L/mol) are nearly identical at C_D/C_T values of 15 and 97.

The spectra of **8A**–, **8B**–, and **8C**–TCNE (Figure 13) have values of λ_1 (400, 390, and 400 nm) that are nearly identical with those of **7A**–TCNE (390 nm), indicating that the λ_1 bands arise from independent $a_2 \rightarrow \pi^*$ transitions in each of the phenyl rings which are not influenced by the ethylenic group. This assignment is supported by the PES study of Güsten et al.,[47] who obtained IE values of 9.03, 8.94, and 9.06 eV for the a_2-like orbitals of **8A**, **8B**, and **8C**. When these values are substituted into eq 1′, they yield λ_1 values of 409, 419, and 405 nm for **8A**–, **8B**–, and **8C**–TCNE which agree favorably with the experimental values.

The λ_2 values of **8A**–, **8B**–, and **8C**–TCNE (510, 530, and 595 nm) are not only different from each other but also strikingly different from that of **7A**–TCNE (480 nm) as well. The differences in λ_2 values of **8B**– and **8C**–TCNE (530 and 595 nm) can be accounted for by assuming that the *cis*-diphenyl groups in **8B** do not achieve coplanarity because they interact sterically, whereas the more widely separated *trans*-diphenyl groups of **8C** do achieve coplanarity. This conjecture is supported by the PES study of Maier and Turner,[42] who estimated interplanar angles of 35° and 0° for **8B** and **8C**. The λ_2 value of **8A**–TCNE relative to that of **7A**–TCNE indicates that the b_1-like orbitals of each of the phenyls conjugates with the π_e orbital to form an extended π orbital. However the steric interference between the *gem*-diphenyls prevents them from simultaneously attaining the coplanar configuration required for optimal conjugation. This interpretation is also supported by the PES study of **8A** by Maier and Turner,[42] which yields an angle of 40° between the planes of the ethylenic and phenyl groups.

When the IE values of Güsten et al.[47] for the b_1-like orbitals of **8A**, **8B**, and **8C** (8.23, 8.11, and 7.79 eV) are substituted into eq 1′, they yield λ_2 values of 520, 542, and 610 nm for **8A**–, **8B**–, and **8C**–TCNE, which compare favorably with the trend in experimental values of 510, 530, and 595 nm. We conclude that the λ_2 value of **8A**–TCNE (595 nm) is characteristic of the condition of optimal b_1–π_e–b_1 conjugation in diphenylethylenes and that the lesser values of λ_2 obtained for **8A**– and **8B**–TCNE are symptomatic of conjugation inhibited by steric interactions of *gem*- and *cis*-phenyls.

b. *N*-Benzylideneaniline and Azobenzene. These compounds, each containing doubly bound nitrogen, are included in the discussion at this point because they are isoelectronic and isostructural with the 1,2-diphenylbenzenes.

The spectrum of **8D**–TCNE consists of a single band with λ_{max} 495 nm, which corresponds closely to an ionization peak in the PE spectrum of **8D** at 8.27 eV that Goetz et al.[48] attributed to the MO resulting from π_e–b_1 conjugation. Reliable values of ϵ (228) and K (3.08 L/mol) are obtained only when TCNE is used in excess. The high value of K is characteristic of TCNE complexes of nitrogen-containing aryls.

Therefore it is surprising that spectra of mixtures of azobenzene and TCNE in DCM at a variety of concentrations and concentration ratios show no evidence of complex formation between 400 and 900 nm, although a band at 480 nm is expected on the basis of the IE value for azobenzene of 8.46 eV reported by Kobayashi et al.[49]

c. Ditolylethylenes. The compounds **8E** and **8F** are of interest because of their structural relationship with **8A**. The spectrum of **8E**–TCNE consists of a strongly skewed band with λ_{max} 435 nm which resolves into two bands λ_1 425 nm and λ_2 510 nm. The value of λ_1 for **8E**–TCNE, which is about 30 nm higher than λ_1 of **8A**–TCNE (λ_1 395, λ_2 510 nm), indicates that the *o*-methyl of **8E** releases

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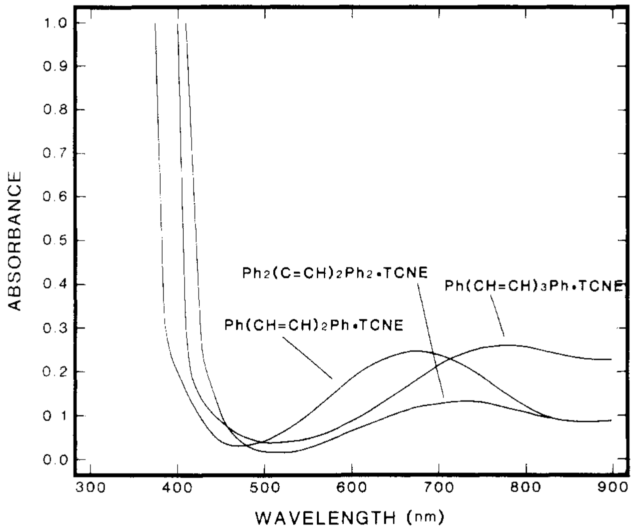

Figure 14. Spectra of α,ω-polyphenylpolyene–TCNE complexes.

electrons primarily to the a_2 orbital.

The spectrum of 8F–TCNE consists of a shoulder, λ_1 at 400 nm, and a band with λ_2 at 565 nm. The value of λ_2, which is about 55 nm higher than that of λ_2 for 8A–TCNE, indicates that the *p*-methyl of 8F releases electrons primarily to the b_1 orbital. The λ_1 and λ_2 values of both 8E- and 8F–TCNE are in agreement with expectations based on previous results.

d. Iminostilbene. The compound 8G is a derivative of 8B in which the o,o′ positions are joined by an imino bridge. The spectrum of 8G–TCNE consists of a broad band at λ_2 780 nm, which is probably due to n–b_1 conjugation between the nonbonded electron pair (n) of the nitrogen and the benzene rings. There is no evidence for the λ_1 band or for the nature of the interaction of the ethenyl group with the benzene ring since 8G itself has a strong absorbance cutoff at 500 nm. The high *K* value of 8G–TCNE (7.03 L/mol) is characteristic of arylamines.

e. Tri- and Tetraphenylethylene. The values of ϵ and *K* given for 8H- and 8I–TCNE are not highly reliable because they are obtained from solutions that cover a small saturation range. Nevertheless, these figures suggest that 8H and 8I behave much like 8B in their interactions with TCNE. As noted in section 8a, an additional unhindered phenyl attached to the ethenyl carbons of an ethylene derivative increases the λ_2 value its TCNE complex by about 100 nm. The fact that the λ_2 values of 8H–, 8I–, and 8C–TCNE (Figure 13) are nearly identical (595, 600, and 595 nm) indicates that the conjugation between π_e orbital and the b_1 orbitals of the third and fourth phenyls of 8H and 8I are strongly inhibited by steric hindrance. This interpretation is supported by the UV studies of Suzuki[50] and the MO calcualtions of Favini and Simonetta,[51] who estimated interplanar angles of 39° and 48° in 8H and 8I. However, our conclusions are strongly contradicted by the PE studies of Güsten et al.;[47] they recorded IE values of 7.54 and 7.18 eV for 8H and 8I, which suggest that there is no significant effect on orbital energies due to crowding of *gem*-diphenyl groups. Their IE values, when substituted into eq 1′, yield λ_{max} values of 707 and 807 nm for 8H- and 8I–TCNE, which are much higher than our experimental values.

Table IV. Spectral Characteristics of Ph(CH=CH)$_n$Ph–TCNE Complexes in Dichloromethane

code	n	λ_{max}(exptl), nm	I_d,[a] eV	λ_{max}(calcd),[b] nm
6F	0	500	8.32[c]	504
8C	1	580	7.94[d]	576
8J	2	665	7.56[e]	673
8K	3	740	7.33[e]	748
8L	4	>750	7.19[e]	803

[a] Ionization energy of donor molecule from PE spectrum. [b] Calculated from eq 1. [c] Reference 38. [d] Reference 42. [e] Reference 52.

f. *trans*-α,ω-Diphenylpolyenes. It is useful to consider these compounds as part of a series with the formula Ph(CH=CH)$_n$Ph (n = 0, 1, 2, 3, ...). The first two members of this series, 6F and 8C, have been discussed previously. The remaining compounds, 8J, 8K, and 8L form blue or green solutions with TCNE that fade rapidly due to irreversible Diels–Alder reactions. The spectra of 8J- and 8K-TCNE (Figure 14) exhibit broad absorbance curves with maxima at 675 and 775 nm. The absorbance values used in the Scott calculations were obtained by mixing each solution rapidly in a cuvette, plotting the absorbance decay at λ_{max} versus time, and extrapolating absorbance to zero time. The times required for absorbance to decay to one-half intensity for the 8J- and 8K-TCNE systems were about 3 and 1 min, respectively. The color of the 8L–TCNE system fades within a few seconds; however, the initial green color of the solution indicates the presence of 8L–TCNE with λ_{max} > 750 nm. Under the circumstances it was possible to obtain reliable values of ϵ and *K* for 8J–TCNE alone.

Hudson et al.[52] reported IE values of 7.56 and 7.33 eV for 8J and 8K; they attributed each of these ionizations to an extended π orbital formed by the conjugation of all of the π_e and b_1 orbitals in the molecule. Substitution of the above IE values into eq 1′ yields λ_{max} values of 673 and 748 nm for 8J- and 8K-TCNE, which compare favorably with the experimental values 665 and 740 nm. This indicates that the absorbance bands of 8J- and 8K–TCNE arise from transitions involving b_1–π_e–b_1 orbitals.

The data in Table IV show that λ_{max} values of complexes of the first four members of the Ph(CH=CH)$_n$Ph–TCNE series tend to increase uniformly with chain length and that λ_{max} values calculated from IEs agree well with experimental values. However, it is not advisable to extend correlations of λ_{max} with chain length beyond n = 4, for as Hudson et al.[52] have shown, IE values rapidly converge to a limit of 7.0–7.2 eV for higher members of the series.

g. 1,1,4,4-Tetraphenyl-1,3-butadiene. The 8M-TCNE system (Figure 14), in contrast to that of 8J–TCNE, is stable since the two additional phenyls appear to provide enough steric hindrance to completely hinder the Diels–Alder addition. The *K* value of 8M–TCNE (1.80 L/mol) is of the same magnitude as those of complexes of the related conjugated dienes 2I- and 8J–TCNE (1.28 and 2.19 L/mol). The λ_{max} of 8M–TCNE is 730 nm. The fact that this value is only 55 nm higher than λ_{max} for 8J–TCNE indicates that there is inhibition of π_e–b_1 conjugation due to steric interactions between the *gem*-phenyls.

h. Summary and Conclusions. (1) Each of the diphenylethylene–TCNE complexes have two absorbance maxima: λ_1 at 390–400 nm and λ_2 at 510–595 nm, which are attributed to $a_2 \rightarrow \pi^*$ and $b_1 \rightarrow \pi^*$ transitions. The λ_2 values increase as steric interference between the phenyls decrease in the order geminal > cis > trans. The steric trend is dependent upon the ease with which the phenyls can attain coplanarity with ethylenic carbons to facilitate π_e–b_1 conjugation.

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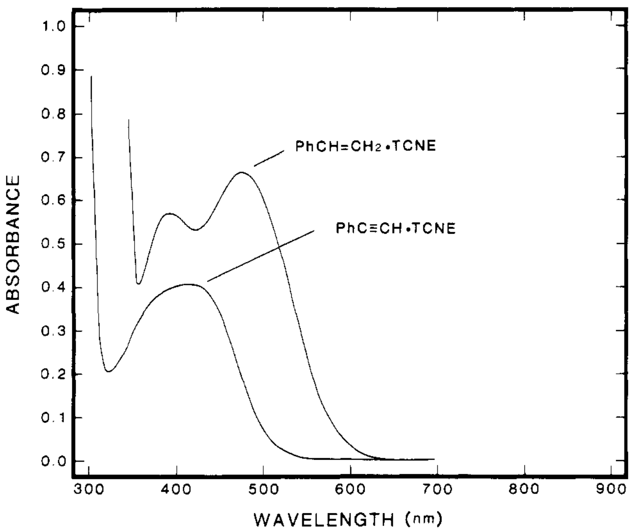

Figure 15. Spectra of styrene–TCNE and phenylethyne–TCNE.

(2) The α,ω-diphenylpolyalkene–TCNE complexes have one absorbance maximum above 675 nm, which is attributed to transitions arising from the π_e–b_1 conjugated orbitals. The λ_{max} values of these complexes increase as the number of conjugated double bonds, *n*, increases when *n* = 0, 1, 2, and 3.

(3) The rate of reaction of TCNE with the α,ω-diphenyl- and α,α,ω,ω-tetraphenylalkenes increases with *n* and decreases with phenyl substitution.

9. Phenylalkynes. In the following discussion the TCNE complexes of **9A**, **9B**, **9C**, and **9D** are compared with those of the cognate phenylethylenes **7A**, **7K**, **8C**, and **8J**. Although evidence for the formation of **9A**–, **9B**–, **9C**–, and **9D**–TCNE was observed, it was not possible to obtain definitive values of ε and *K* for any of these complexes.

a. Monoalkynes. The spectrum of **9A**–TCNE (Figure 15) consists of a skewed band with λ_{max} 420 nm which resolves into strongly overlapping bands with maxima λ_1 and λ_2 at about 370 and 435 nm. The spectrum of **9B**–TCNE (Figure 6) has distinct bands with maxima at 365 and 475 nm; **9C**–TCNE (Figure 16) has a shoulder at 365 nm and a band at 520 nm. In each of these complexes λ_1 is at 365–370 nm, indicating that this band is due to an $a_2 \rightarrow \pi^*$ transition. The IE values reported by Griebel et al.[53] for the a_2-like orbitals of **9A** and **9B** are 9.48 and 9.38 eV, while that reported by Maier and Turner[42] for **9C** is 9.30 eV. When these IE values are substituted into eq 1′, they yield λ_1 values of 365, 374, and 381 nm for **9A**–, **9B**–, and **9C**–TCNE, which are in good agreement with the experimental values of 370, 365, and 365 nm. That these λ_1 values are about 25–35 nm lower than the λ_1 values for the corresponding phenylethylene–TCNE complexes, **7A**–, **7K**–, and **8C**–TCNE (395, 400, and 400 sh nm) is due to the ability of an ethynyl α-carbon to withdraw electrons from the π orbitals of the phenyl ring through induction.

The trend in λ_2 values for **9A**–, **9B**–, and **9C**–TCNE (435, 475, and 525 nm) roughly parallels the trend in λ_2 values for **7A**–, **7K**–, and **8C**–TCNE (480, 530, and 595 nm) but at values that are 45, 55, and 75 nm lower. The IE values of the b_1-like orbitals of **9A** and **9B** reported by Griebel et al.[53] (8.78 and 8.49 eV) and of **9C** by Maier and Turner[42] (8.84 eV) when substituted into eq 1′ yield λ_2 values for **9A**–, **9B**–, and **9C**–TCNE of 438, 477, and 551 nm, which agree favorably with the experimental values of 435, 475, and 525 nm. These observations indicate that the b_1-like orbitals of **9A**, **9B**, and **9C** are conjugated with the π_e orbitals of the ethynyl group and that they are subject to the inductive electron-withdrawing effect of the α-carbon atom as well.

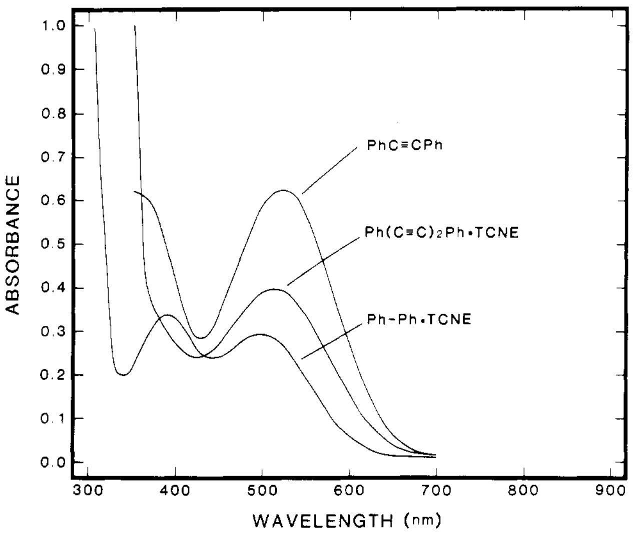

Figure 16. Spectra of biphenyl–TCNE and diphenylalkyne–TCNE complexes.

b. Diphenylbutadiyne. The spectrum of **9D**–TCNE (Figure 16) consists of a shoulder at 375 nm and a broad band at 510 nm. The λ_1 value is nearly identical with that of **9C**–TCNE (365 nm), indicating that the λ_1 band arises from an $a_2 \rightarrow \pi^*$ transition and that the α-carbon of the butadiynyl group withdraws electrons from the phenyl rings. Andreocci et al.[54] reported an ionization band in the PE spectrum of **9D** at 9.48 eV. This value, when substituted into eq 1, yields a λ_1 value of 365 nm for **9D**–TCNE, which is in good agreement with the experimental value at 375 nm.

The λ_2 band of **9D**–TCNE at 510 nm has a width $\Delta\nu_{1/2}$ of 6300 cm^{-1} compared to corresponding values for **9C**–TCNE of 520 nm and 5800 cm^{-1}. The fact that λ_2 for **9D**–TCNE is smaller than that for **9C**–TCNE is surprising in view of the results obtained with **8C**– and **8J**–TCNE. However, Andreocci et al.[54] report three closely spaced ionization bands in the PE spectrum of **9D** at 8.23, 8.55, and 8.87 eV; the first two were attributed to the conjugated b_1–π_e system which extends over the entire molecule and the third to the π_e orbitals. These IEs yield λ values of 520, 469, and 427 nm for **9D**–TCNE when substituted into eq 1′. We can account for the position and width of the λ_2 band by assuming that it arises primarily from transitions involving the top two orbitals of **9D** with a weak contribution from the third orbital.

c. Summary and Conclusions. The spectra of the phenylalkyne–TCNE complexes exhibit two maxima between 365 and 520 nm.

(1) Each of these complexes exhibits λ_1 at 365 nm which arises from an $a_2 \rightarrow \pi^*$ transition. The λ_1 values of the phenylalkyne–TCNE bands are 25–35 nm lower than those of the corresponding phenylalkene–TCNE complexes because of the strong electron-withdrawing effect of the ethylynic α-carbon.

(2) The λ_2 bands of the phenylalkyne–TCNE complexes arise from transitions originating in the conjugated π_e–b_1 donor orbitals. The trend in λ_2 values of the phenylalkyne–TCNE complexes roughly parallels the trend in λ_2 values for the corresponding phenylalkene–TCNE com-

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plexes but at values that are 45–75 nm lower.

(3) The λ_2 value for **9D**–TCNE (510 nm) is lower than that of **9C**–TCNE (520 nm), indicating the absence of conjugation through the double bonds in **9D**. This conclusion contrasts with that made for **3F**, which shows evidence of conjugation.

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Registry No. **1A**·TCNE, 123884-13-9; **1B**·TCNE, 123884-14-0; **1C**·TCNE, 123884-15-1; **1D**·TCNE, 123884-16-2; **1E**·TCNE, 123884-17-3; **2A**·TCNE, 93245-61-5; **2B**·TCNE, 123884-18-4; **2C**·TCNE, 123884-19-5; **2D**·TCNE, 51930-60-0; **2E**·TCNE, 123884-20-8; **2F**·TCNE, 36880-85-0; **2G**·TCNE, 123884-21-9; **2H**·TCNE, 93758-83-9; **2I**·TCNE, 52515-79-4; **2J**·TCNE, 61822-51-3; **2K**·TCNE, 123884-22-0; **2L**·TCNE, 123884-23-1; **3A**·TCNE, 123884-24-2; **3B**·TCNE, 123884-25-3; **3C**·TCNE, 123884-26-4; **3D**·TCNE, 123884-27-5; **3E**·TCNE, 123884-28-6; **3F**·TCNE, 123884-29-7; **3G**·TCNE, 123884-30-0; **4A**·TCNE, 1446-08-8; **4B**·TCNE, 6165-98-6; **5A**·TCNE, 2590-60-5; **5B**·TCNE, 18852-73-8; **5C**·TCNE, 26515-97-9; **5D**·TCNE, 26819-20-5; **5E**·TCNE, 17557-14-1; **5F**·TCNE, 2590-61-6; **5G**·TCNE, 2590-62-7; **5H**·TCNE, 2590-63-8; **5I**·TCNE, 123884-31-1; **5J**·TCNE, 26034-90-2; **5K**·TCNE, 2590-64-9; **5L**·TCNE, 2590-65-0; **5M**·TCNE, 123884-32-2; **5N**·TCNE, 2590-66-1; **5O**·TCNE, 123884-33-3; **5P**·TCNE, 26034-91-3; **5Q**·TCNE, 2590-68-3; **5R**·TCNE, 2590-69-4; **5S**·TCNE, 1223-67-2; **5T**·TCNE, 962-69-6; **5U**·TCNE, 2605-01-8; **5V**·TCNE, 78717-32-5; **5W**·TCNE, 123884-34-4; **5X**·TCNE, 123884-35-5; **6A**·TCNE, 62371-33-9; **6B**·TCNE, 123884-36-6; **6C**·TCNE, 70239-05-3; **6D**·TCNE, 123884-37-7; **6E**·TCNE, 51644-54-3; **6F**·TCNE, 6140-60-9; **6G**·TCNE, 2987-74-8; **6H**·TCnE, 123884-38-8; **7A**·TCNE, 7431-42-7; **7B**·TCNE, 123884-39-9; **7C**·TCNE, 33429-76-4; **7D**·TCNE, 33429-74-2; **7E**·TCNE, 123884-40-2; **7F**·TCnE, 123884-41-3; **7G**·TCNE, 123884-42-4; **7H**·TCNE, 123884-43-5; **7I**·TCNE, 123884-44-6; **7J**·TCNE, 53039-88-6; **7K**·TCNE, 123884-45-7; **7L**·TCNE, 123884-46-8; **7M**·TCNE, 123884-47-9; **7N**·TCNE, 7378-72-5; **7O**·TCNE, 123884-48-0; **7P**·TCNE, 123884-50-4; **7Q**·TCNE, 123884-51-5; **8A**·TCNE, 60977-89-1; **8B**·TCNE, 7371-39-3; **8C**·TCNE, 7371-38-2; **8D**·TCNE, 108461-13-8; **8E**·TCNE, 123884-52-6; **8F**·TCNE, 123884-53-7; **8G**·TCNE, 123884-54-8; **8H**·TCNE, 60977-90-4; **8I**·TCNE, 60977-91-5; **8J**·TCNE, 19255-32-4; **8K**·TCNE, 123884-55-9; **8L**·TCNE, 123884-56-0; **8M**·TCNE, 123884-57-1; **9A**·TCNE, 29578-48-1; **9B**·TCNE, 29578-50-5; **9C**·TCNE, 62371-37-3; **9D**·TCNE, 123884-58-2.

(Diphenylphosphinoyl)oxyl: An Extremely Reactive Oxygen-Centered Radical[1]

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The title radical, $Ph_2P(O)O^{\bullet}$, has been generated by laser flash photolysis (LFP) of the peroxide $[Ph_2P(O)O]_2$ (**1**) in CH_3CN solution. It has a broad, structureless absorption extending from 400 to beyond 800 nm. Absolute bimolecular rate constants k for its reactions with various organic substrates have been measured by LFP. It has been found that $Ph_2P(O)O^{\bullet}$ is more reactive in hydrogen abstraction (e.g., cyclohexane, $k = 2.4 \times 10^8$ M^{-1} s^{-1}) and addition (e.g., benzene, $k = 9.1 \times 10^8$ M^{-1} s^{-1}) than any other organic oxygen-centered radical. Only $HO^{\bullet}$ is (generally) more reactive. Although $Ph_2P(O)O^{\bullet}$ could not be directly detected by EPR spectroscopy, it was successfully spin-trapped with a nitrone and with alkenes and alkynes. The formation of $Ph_2P(O)O^{\bullet}$ in the photodecomposition but not in the thermal decomposition of **1** is supported by ^{31}P NMR analyses of reaction products. Semiempirical AM1–PM3 calculations on $H_2P(O)O^{\bullet}$ are also reported.

Absolute rate constants for the reactions of several classes of carbonyloxyl radicals, $XC(O)O^{\bullet}$, with a variety of organic substrates have recently been measured in this laboratory by using the technique of laser flash photolysis (LFP).[3-6] The magnitude of the second-order rate constant for hydrogen atom abstraction and/or addition reactions of $XC(O)O^{\bullet}$ with a specific substrate generally increased with an increase in the inductive electron-withdrawing effect of the substituent X.[4-7] Differences in the reactivities of different $XC(O)O^{\bullet}$ were attributed to variations in the relative contribution that polar, canonical structures (e.g., $[XC(O)O^-,RH^{\bullet+}]^{\ddagger}$) make to the stabilization of the reaction's transition state.[4-6] It therefore seemed possible that oxyl radicals even more reactive than the $XC(O)O^{\bullet}$ already examined[7] might be derived from oxy acids having greater intrinsic (i.e., gas phase) acidities[8] than the intrinsic acidities of the XC(O)OH acids. An attractive possibility for a preliminary test of this hypothesis was the (diphenylphosphinoyl)oxyl radical, $Ph_2P(O)O^{\bullet}$,[9] since the

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(1) Issued as NRCC No. 30772. This paper is dedicated to the memory of the late Professor A. Mangini, University of Bologna, Italy.

(2) NRCC/Summit Postdoctoral Fellow, 1987–1988.

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(7) X = aryl,[4] alkoxy,[5] alkenyl,[6] and alkynyl.[6]

(8) As measured by ΔG for the gas-phase reaction: $HA \rightarrow H^+ + A^-$.

(9) The structure is written as $Ph_2P(O)O^{\bullet}$ rather than $Ph_2PO_2^{\bullet}$ in order to distinguish this radical from its (unknown) peroxyl isomer, $Ph_2POO^{\bullet}$.

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