J. Org. Chem. 1992, 57, 6460–6466

Charge-Transfer Complexes of Tetracyanoethylene with Alkyl- and Alkenylnaphthalenes and Related Compounds

John E. Frey,* Anne M. Andrews, Scott D. Combs, Steven P. Edens, Jeffrey J. Puckett, Ronald E. Seagle, and Lori A. Torreano

Department of Chemistry, Northern Michigan University, Marquette, Michigan 49855

Received May 29, 1992

Spectral characteristics, λ_{max} and ϵ, and equilibrium constants, K, for charge-transfer complexes of tetracyanoethylene (TCNE) with alkyl-substituted naphthalenes in dichloromethane are presented. Values of ϵ and K generally increase with alkyl substitution. All complexes exhibit two or three absorbance bands λ_1 550–885 nm, λ_2 425–585 nm, and λ_3 330–440 nm which are due to charge-transfer transitions from the three highest π orbitals of the naphthalene ring to the π^* orbital of TCNE. Unhindered α- and β-methyl substituents produce wavelength shifts of 36 and 25 nm per methyl in λ_1 and of 5 and 26 nm per methyl in λ_2 relative to naphthalene–TCNE (λ_1 550, λ_2 430 nm). Wavelength shifts are correlated with corresponding shifts in ionization energies of the methylnaphthalenes and with the symmetries of the π donor orbitals. The wavelength shifts successfully predict λ_1 and λ_2 values of polymethylnaphthalenes without hindered methyls, indicating that the shifts are additive. The effects of *peri*-dimethyl steric interactions in naphthalenes on λ_{CT} values and the characteristics of complexes of TCNE with perylene, azulene, and some biphenylenes and bicycloalkenes are also presented.

Introduction

Merrifield and Phillips[1] first reported that the spectrum of a solution of tetracyanoethylene (TCNE) and naphthalene (N) in dichloromethane (DCM) exhibited two bands, λ_1 550 and λ_2 429 nm (Figure 1). They attributed the two bands to charge-transfer (CT) transitions arising from $\pi^* \leftarrow \pi$ electron transfers between the HOMOs of N and the LUMO of TCNE of the complex N–TCNE. When N and T collide in solution they form a complex, N–T, in which the HOMO is associated with N and the LUMO is associated with T. If a photon of visible light with sufficient energy to promote an electron from the HOMO to the LUMO interacts with the complex, a short-lived ion pair, N^+T^-, forms with the simultaneous absorption of a quantum $h\nu$. This process can be represented by a two-stage equilibrium of which the second step is very rapid.

$$N + T \rightleftharpoons N\text{–}T \overset{h\nu}{\rightleftharpoons} N^+T^-$$

The formation constant for the complex is given by the equation

$$K = [N\text{–}T]/[N][T] \qquad (1)$$

The spectrum of this system exhibits two CT bands in UV–vis region; however the characteristic absorbance bands of T^- are not observed because of the fleeting existence of the ion pair.

The N–TCNE system has often served as a model to elucidate the general nature of CT complexes as shown by the following examples. Johnson and Bowen[2] found it necessary to assume the presence of complexes of two different stoichiometries, NT and N_2T, to explain the variation of K values with respect to the wavelength in N/TCNE/CCl_4 systems. Bendig et al.[3] showed that $K(\text{obs}) \approx 0.85K(\text{NT})$ and $K(N_2T) \approx 0.1K(\text{NT})$. The presence of 2:1 complexes has since been confirmed in numerous systems.

Studies of the N–TCNE system reported by Kuroda et al.,[4] Mayoh and Prout,[5] and Mobley et al.[6] indicate that the conformations of minimum energy for N–TCNE correspond to that of maximum $\pi(\text{HOMO})$-π^* overlap. This conclusion is in agreement with the results of the X-ray diffraction study of crystalline N–TCNE of Williams and Wallwork[7] which shows that the component molecules are stacked alternately in columns at a separation of 330 pm supporting the existence of a weak bonding interaction between N and TCNE. This finding has been applied to interactions in other donor–TCNE complexes generally.

The assignment of the multiple spectral bands of N–TCNE to transitions from the two HOMOs of N is supported by the work of Eland and Danby[8] who show that the photoelectron bands of N at 8.12, 8.90, and 10.00 eV correspond to ionizations from the a_u, b_{1u}, and b_{2g} orbitals (Figure 2). In general the relationship between λ_{CT} values of donor–TCNE complexes with I_D values taken from the PE spectra of the donor molecules is given by eq 2

$$\lambda_{CT}\ (\text{nm}) = 1240\ (\text{eV-nm})/(0.81I_D - 4.28) \qquad (2)$$

where λ_{CT} is the wavelength of maximum absorbance of the CT band, I_D is the vertical ionization energy (eV) of the corresponding orbital of the donor molecule taken from PE spectra, and 0.81 and 4.28 are empirical parameters for donor–TCNE systems.[9] The first two ionizations in the PE spectrum of N yield CT values of 529 and 428 nm for N–TCNE which are in excellent agreement with the reported values of 550 and 429 nm.

In view of the unique role of N–TCNE as a model system we have proceeded with a comprehensive study of the interactions of TCNE with a variety of naphthalene derivatives and related polycyclic hydrocarbons. This investigation, a continuation of systematic studies of TCNE complexes of hydrocarbons,[10] reports the characteristics of the complexes of TCNE with alkylnaphthalenes as well as perylene, azulene, and some related biphenylenes and cycloalkenes.

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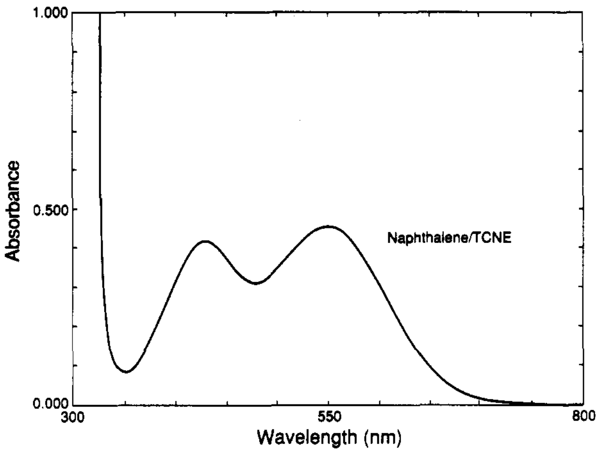

Figure 1. Spectrum of naphthalene–TCNE.

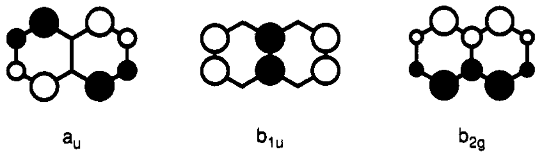

Figure 2. Highest molecular orbitals of naphthalene.

The specific objectives of this work are to determine (1) the effects of multiple alkyl substitution on the formation constants (K) and absorbance maxima (λ_{CT}) of the CT bands of complexes of TCNE with naphthalene derivatives, (2) the effects of *peri*-dimethyl steric interactions and ring distortions in naphthalenes on λ_{CT}, (3) the specific donor orbitals which give rise to CT interactions between TCNE with naphthalenes and related polycyclic compounds, and (4) selected characteristics of CT complexes of TCNE with perylene, azulene, and some biphenylenes and bicycloalkenes.

Experimental Section

The experimental procedures, data collection and processing, and judgmental criteria are described in a previous publication.[10] Spectra of complexes with absorbance bands extending beyond 800 nm were recorded with a Shimadzu UV3101PC spectrophotometer.

Results and Discussion

The data obtained from this study are summarized in Table I. Donors are coded for reference in the text according to the alphanumeric characters shown in column 1. TCNE complexes of naphthalene derivatives usually exhibit two well-defined CT bands plus a shoulder on the naphthalene cutoff which most often occurs at 325–350 nm. Complexes of some polymethylated naphthalenes however exhibit a third band with a distinct maximum. Wavelength maxima for these CT bands, designated λ_1, λ_2, and λ_3, are shown in columns 3–5. If the band appears as a shoulder on the solute cutoff, the wavelength at half band height is given with an "sh" suffix.

Molar absorbance values, ϵ_{max}, for the band with the greatest absorbance is given in column 6. The ratios of absorbances of λ_2 or λ_3 to λ_1, A_2/A_1 or A_3/A_1, are given in column 7 and the band height at half-width, $\Delta\nu_{1/2}$, is given in column 8. The apparent association constant, K (L/mol), for the complex is reported in column 9. The product "ϵK", given in column 10, is a measure of the "effective absorbance" of a complex since the larger the value of ϵ and/or K, the greater is the net absorbance of the complex for given levels of reagent concentrations. The ϵK values are of interest because their magnitudes are characteristic of the various classes of complexes; in some cases trends in ϵK values follow progressive structural modifications in substituent groups.

The ratios of the concentrations of stock solutions of the donor, C_D, and of TCNE, C_T, are given in column 11. When C_D is larger than C_T the ratio C_D/C_T is presented as an integer; when TCNE is used in excess C_D/C_T is presented as a fraction. The stock solutions are normally mixed in ratios ranging from 9:1 to 1:1 in order to produce a series of solutions where one reagent is present in large excess over the other.

The saturation fraction, s, of a complex, that is the molar concentration of the complex divided by the concentration of the limiting reactant, is calculated using the equation $s = A/\epsilon C_Y$ where C_Y is the analytical concentration of the limiting reagent. Percent saturation values are given in column 12.

1. **Naphthalene.** The optical spectrum of the N–TCNE system (Figure 1) consists of two bands with maxima at λ_1 550 and λ_2 430 nm with a sharp donor cutoff at 330 nm due to N. The first two bands in the PE spectrum of N arise from ionizations at I_1 8.18 and I_2 8.86 eV,[8] which correspond to CT values of 529 and 428 nm. The bands in the N–TCNE spectrum arise from the CT transitions $\pi^* \leftarrow a_u$ and $\pi^* \leftarrow b_{1u}$ between N and TCNE. The I_3 value of N at 10.07 eV yields a CT wavelength of 320 nm which is covered by the cutoff at 330 nm. The fact that K values of 1.13 and 0.63 L/mol are obtained at C_D/C_T ratios of 20 and 305 indicates the presence of both NT and N_2T species in solutions with a large excess of donor. The higher K value, 1.13 L/mol, deemed a more accurate estimate of the true value for N–TCNE, is in good agreement with previously reported values.

Structural studies of N by both X-ray[11] and neutron[12] diffraction indicate that the molecule is planar with D_{2h} symmetry. This model serves as a basis of comparison for naphthalene derivatives in the subsequent discussion.

2. **Monoalkyl- and Monoalkenylnaphthalenes.** The spectra of the 1M–TCNE and 2M–TCNE systems each consist of two well-defined bands with evidence for a third band at the donor cutoff. Both systems yield K values which decrease with increasing C_D/C_T, indicating the presence of both DT and D_2T species in solutions containing excess donor.

Before proceeding with the analysis of the spectra of the complexes of the alkynaphthalenes it is useful to refer to a summary of data from the PE study of Heilbronner et al.[13] (Table II) concerning the inductive effects of methyl substituents on the ionization energies of the a_u and b_{1u} orbitals of the naphthalene ring. This study shows that unhindered methyl groups in the α and β positions cause a mean decrease of 0.17 eV per methyl in I_1 and that the methyls appear to interact independently and additively. They attribute the uniform decrease to the presence of an antinode on the a_u orbital in both positions. However an unhindered methyl in the α position produces a mean decrease of only 0.09 eV per methyl on I_2 compared to a β-methyl which produces a mean decrease of 0.19 eV. They attribute the small inductive effect of the α-methyl on the energy of the b_{1u} orbital to the location of the nodes of this orbital at the α position.

The spectrum of 1M–TCNE consists of three bands λ_1 585, λ_2 434 and λ_3 345 sh nm. The PE bands of 1M at 8.01,

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Table I. Complexes of TCNE with Naphthalenes and Related Compounds in Dichloromethane at 22 °C

code	donor compound	λ_1, nm	λ_2, nm	λ_3, nm	ϵ_{max}, L/mol-cm	A_2,A_3/A_1	$\Delta\nu_{1/2}$, cm^{-1}	K, L/mol	ϵK	C_D/C_T	% satn
N	naphthalene	550	430		845 ± 45	0.89		1.13 ± 0.06	960	20	8–18
	naphthalene	553	431		1420 ± 70	0.91		0.63 ± 0.03	780	305	18–33
	naphthalene[a]	550	429		1240	0.90		0.70	870		
	naphthalene[b]	553	429			0.92					
	naphthalene[c]	560	430								
	naphthalene[d]	553	433								
	naphthalene[e]	553	429								
	naphthalene[f]	550									
	naphthalene[g] (calorimetric)							0.2437 ± 0.0022			
	naphthalene[h] (in $CHCl_3$)	558	432		2001 ± 107	0.86		1.05 ± 0.09	2100		
	naphthalene[i] (in $CHCl_3$)	550	430		1600			1.01 ± 0.04	1620		
	naphthalene[j] (in $CHCl_3$)										
	NT	560	430		1520 ± 50	0.93		1.19 ± 0.04	1810		
	N_2T	550	420		2110 ± 700	0.76		0.15 ± 0.05	320		
	naphthalene[b] (in CCl_4)	550	430		1635			3.27	5350		
	naphthalene[k] (in CCl_4)	550	427			0.86					
1M	1-methylnaphthalene	584	437	330 sh	890 ± 170	0.86, 0.77		1.71 ± 0.31	1520	1/10	5–11
	1-methylnaphthalene	585	435		1420 ± 70	0.86		0.82 ± 0.02	1480	24	9–19
	1-methylnaphthalene	580	435		1810 ± 40	0.85		0.82 ± 0.02	1480	200	18–34
	1-methylnaphthalene[d]	588	439								
1E	1-ethylnaphthalene	590	438	350 sh	1270 ± 110	0.83		1.10 ± 0.10	1400	10	5–10
	1-ethylnaphthalene	589	438	350 sh	1300 ± 180	0.83		1.17 ± 0.17	1520	29	10–20
1B	1-*tert*-butylnaphthalene[l]	592	438		715	0.52					10–20
2M	2-methylnaphthalene	575	455		1520 ± 100	0.89		1.07 ± 0.07	1630	20	7–15
	2-methylnaphthalene	575	455		2170 ± 60	0.89		0.68 ± 0.02	1480	566	20–36
	2-methylnaphthalene[d]	575	461								
	2-methylnaphthalene[f]	578									
2E	2-ethylnaphthalene	580	460		573 ± 71	0.92		2.90 ± 0.36	1660	1/8	8–17
1V	1-vinylnaphthalene*[m]	603	432								
2V	2-vinylnaphthalene*	580	465		1590 ± 50	0.96		0.68 ± 0.02	1080	20	6–14
12M	1,2-dimethylnaphthalene	615	460	350 sh	1790 ± 150	0.81		1.54 ± 0.13	2760	1/10	4–9
13M	1,3-dimethylnaphthalene	613	462	335 sh	1730 ± 230	0.81		1.44 ± 0.22	2490	1/10	4–9
	1,3-dimethylnaphthalene	605	455	335 sh	1950 ± 160	0.80		1.42 ± 0.12	2770	20	7–15
	1,3-dimethylnaphthalene	611	463	335 sh	2060 ± 90	0.82		1.35 ± 0.06	2800	96	14–20
14M	1,4-dimethylnaphthalene	615	440	330 sh	1140 ± 60	0.74		2.52 ± 0.13	2870	1/10	7–15
	1,4-dimethylnaphthalene	621	442	330 sh	1690 ± 60	0.74		1.71 ± 0.06	2890	99	17–31
14B	1,4-di-*tert*-butylnaphthalene[l]	626	445		47	1.12				10–20	
15M	1,5-dimethylnaphthalene	617	442	352	2570 ± 340	0.90, 0.65		0.83 ± 0.11	2130	1/10	3–6
16M	1,6-dimethylnaphthalene	610	463	338	1180 ± 80	0.81, 0.57		1.78 ± 0.11	2100	1/8	5–11
18M	1,8-dimethylnaphthalene	636	441	344 sh	2070 ± 550	0.80, 0.58	4600, 5100	1.15 ± 0.05	2380	1/10	3–7
	1,8-dimethylnaphthalene	630	440	360 sh	1590 ± 50	0.80		1.54 ± 0.05	2450	20	7–16
23M	2,3-dimethylnaphthalene	595	491	350 sh	2100 ± 550	0.95		1.46 ± 0.38	3070	1/10	4–9
26M	2,6-dimethylnaphthalene	600	475		110 ± 70	0.88		2.73 ± 0.19	3000	20	13–27
26B	2,6-di-*tert*-butylnaphthalene	620	490		1690 ± 40	1.08		0.63 ± 0.02	1070	25	6–12
	2,6-di-*tert*-butylnaphthalene[l]	620	487		572	1.11				10–20	
27M	2,7-dimethylnaphthalene	597	492		1320 ± 150	0.95		1.94 ± 0.29	2560	1/10	6–13
27B	2,7-di-*tert*-butylnaphthalene[l]	610	501		625	0.89				10–20	
ANT	acenaphthene*	651	443	335 sh	912 ± 73	0.76, 0.50	4500, 4700	2.76 ± 0.22	2520	1/10	8–17
	acenaphthene*	655	450	335 sh	1980 ± 90	0.74	4500, 4800	1.24 ± 0.06	2460	16	7–15
	acenaphthene*[c]	655	440								
	acenaphthene*[e]	645	441								
	acenaphthene*[g]							0.4254 ± 0.0010			
ANL	acenaphthylene	505			1830 ± 90			1.30 ± 0.06	2380	1/10	4–9
	acenaphthylene	510			1550 ± 100		9100	1.64 ± 0.10	1540	20	8–17
	acenaphthylene[m]	510					7800				
	acenaphthylene[h] (in $CHCl_3$)	515			2180 ± 117			2.84 ± 0.18	6190		
235M	2,3,5-trimethylnaphthalene	630	495	345	2090 ± 190	0.95, 0.56		2.04 ± 0.18	4260	1/8	6–13
HHP	1,2,3,6,7,8-hexahydropyrene	751	460	405	1530 ± 70	0.70, 0.67	4300	2.23 ± 0.26	3410	1/10	7–14
HXM	1,2,3,4,5,8-hexamethylnaphthalene	796	490 sh	415 sh							
HPM	1,2,3,4,5,6,7-heptamethylnaphthalene	771	566	400	159 ± 13	0.57, 0.83		135 ± 89	21500	1/15	82–88
	1,2,3,4,5,6,7-heptamethylnaphthalene	772	565	400	189 ± 13	0.60, 0.73		60 ± 15	11300	1/39	73–85
OCM	octamethylnaphthalene	885	582	438	125 ± 2	0.70, 0.74		40.8 ± 1.2	5100	1/17	56–75
PRL	perylene	890			1440 ± 140		4100	3.45 ± 35	4970	1/13	10–20
	perylene[c]	900									
	perylene[n] (in $CHCl_3$)	920									
	perylene[h] (in $CHCl_3$)	915			6174 ± 4917			4.03 ± 1.39	25000		
BPL	biphenylene	677	412 sh		3100 ± 1000		4500	0.89 ± 0.29	2760	1/10	3–6
	biphenylene[o]	680			500 ± 50			5.1 ± 0.5	2600	1/100	
	biphenylene[p]	680			3290 ± 30			0.71 ± 0.01	2340	1	
18MB	1,8-dimethylbiphenylene[o]	715			1670 ± 170			6.4 ± 0.6	10700	1/100	
27MB	2,7-dimethylbiphenylene[o]	765			1160 ± 120			8.5 ± 0.6	9800	1/100	
OMB	octamethylbiphenylene	875	560		1490 ± 10	0.15	3900	411 ± 30	612000	1/21	85–92
AZL	azulene	686	470 sh		3590 ± 290	0.26	4700	10.01 ± 0.94	36000	1/81	24–42
	azulene[c]	630									
	azulene[n] (in $CHCl_3$)	740									
	azulene[h] (in $CHCl_3$)	735						14.60 ± 0.95			
	azulene[q] (in $CHCl_3$)	740									
CHX	cyclohexene[r]	415			cur		6900			20	

Table I (Continued)

code	donor compound	λ_1, nm	λ_2, nm	λ_3, nm	ϵ_{max}, L/mol-cm	A_2,A_3/A_1	$\Delta\nu_{1/2}$, cm^{-1}	K, L/mol	ϵK	C_D/C_T	% satn
BHP	bicyclo[2.2.1]-2-heptene[r]	430			neg		6700			20	
CHXD	1,4-cyclohexadiene	440	340		279 ± 17	0.96		0.46 ± 0.03	130	10	
BHPD	bicyclo[2.2.1]hepta-2,5-diene	470	385		412 ± 25	1.50		0.18 ± 0.01	74	20	6–13

*Reacts with TCNE. [a] Reference 1. [b] Briegleb, G.; Czekalla, J.; Reuss, G. *Z. Physik. Chem.* (*Wiesbaden*) **1961**, *30*, 316–332. [c] Reference 4. [d] Sakurai, H.; Kira, M. *J. Am. Chem. Soc.* **1974**, *96*, 791–794. [e] Ponec, R.; Chernyshev, E. A.; Tolstikova, N. G.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2714–2717. [f] Lopatin, M. A.; Kuznetsov, V. A.; Muslin, D. A.; Egorochkin, A. N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1980**, *50*, 2222–2226; *Zh. Obshch. Khim.* **1980**, *50*, 2745–2750. [g] Herndon, W. C.; Feuer, J.; Mitchell, R. E. *Anal. Calor.* **1974**, *3*, 249–281. [h] Reference 23. [i] Cooper, A. R.; Crowne, C. W. P.; Farrell, P. G. *Trans. Faraday Soc.* **1966**, *62*, 18–28. [j] Reference 3. [k] Kuroda, H.; Amano, T.; Ikemoto, I.; Akamatu, A. *J. Am. Chem. Soc.* **1967**, *89*, 6056–6063. [l] Reference 14. [m] Shirota, Y.; Nagata, J.; Nakano, Y.; Nogami, T.; Mikawa, H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 14–18. [n] Dewar, M. J. S.; Rogers, H. *J. Am. Chem. Soc.* **1962**, *84*, 395–398. [o] Reference 25. [p] Reference 24. [q] Luhowy, R.; Keehn, P. M.; *J. Am. Chem. Soc.* **1977**, *99*, 3797–3805. [r] Reference 10.

Table II. Shifts in Vertical Ionization Energies of Methylnaphthalenes as a Function of Methyl Position on Ring

			ΔI_1/Me[a]				ΔI_2/Me[a]	
donor	I_1	ΔI_1	α	β	I_2	ΔI_2	α	β
N[b]	8.18				8.86			
1M[b]	8.01	0.17	0.17		8.81	0.05	0.05	
2M[b]	8.01	0.17		0.17	8.69	0.17		0.17
12M[c]	7.78	0.30	*0.15*	*0.15*	8.53	0.33	*0.11*	*0.22*
13M[b]	7.86	0.32	*0.16*	*0.16*	8.61	0.25	*0.08*	*0.17*
14M[b]	7.82	0.36	0.18		8.69	0.17	0.09	
15M[b]	7.85	0.33	0.17		8.69	0.17	0.9	
16M[c]	7.80	0.38	*0.19*	*0.19*	8.53	0.33	*0.11*	*0.22*
18M[b]	7.64	0.54	0.27[d]		8.60	0.36	0.18[d]	
23M[b]	7.89	0.29		0.15	8.52	0.34		0.17
26M[c]	7.78	0.40		0.20	8.50	0.36		0.18
27M[b]	7.89	0.29		0.15	8.50	0.36		0.18
mean			0.17	0.17			0.09	0.19

[a] Values in italics are estimated. [b] Reference 13. [c] Reference 15. [d] Sterically hindered methyls; not included in mean.

Table III. Shifts in Absorbance Maxima for TCNE Complexes of Methyl- and *tert*-Butylnaphthalenes[b]

			$\Delta\lambda_1$/R[a]				$\Delta\lambda_2$/R[a]	
donor	λ_1	$\Delta\lambda_1$	α	β	λ_2	$\Delta\lambda_2$	α	β
N	550				430			
1M	586	36	36		435	5	5	
2M	575	25		25	455	25		25
12M	615	65	*38*	*27*	460	30	*5*	*25*
13M	616	66	*39*	*27*	460	30	*5*	*25*
14M	615	65	33		440	10	5	
15M	617	67	34		442	6	6	
16M	610	60	*35*	*25*	463	33	*6*	*27*
18M	630	80	40		440	10	5	
23M	595	45		23	491	61		31
26M	600	50		25	475	45		23
27M	597	47		24	492	62		31
mean (for Me)			36	25			5	27
1B	592	42	42		438	8	8	
14B	626	76	38		445	15	8	
26B	620	70		35	487	55		28
27B	610	60		30	501	71		36
mean (*t*-Bu)			40	33			8	32

[a] Values in italics are estimated. [b] Reference 14.

8.81, and 9.76 eV observed by Heilbronner et al.[13] yield calculated λ_{CT} values of 562, 434, and 342 nm, indicating that the CT bands indeed arise from electronic transitions from the three HOMOs of the naphthalene ring. These data (Table III) indicate that an α-Me substituent produces a larger increase in λ_1 and λ_2 for 1M–TCNE relative to N–TCNE. The larger shift, $\Delta\lambda_1$ 36 nm, arises from the strong inductive interaction of the α-Me with a_u. The smaller shift, $\Delta\lambda_2$ 5 nm, arises from the weak inductive interaction of the α-Me with b_{1u}.

The spectrum of 1E–TCNE exhibits bands, λ_1 590, λ_2 438, and λ_3 350 sh, which are similar to those of 1M–TCNE. Evans et al.[14] reported λ_1 and λ_2 values of 592 and 438 nm for 1B–TCNE. The $\Delta\lambda_{CT}$ shifts for the α-ET and α-*t*-Bu groups are slightly larger than the corresponding shifts for the α-Me group, indicating that the inductive effects of Et and *t*-Bu substituents are either greater than that of Me or that Et and *t*-Bu produce distortions in the naphthalene ring arising from steric interactions with the *peri*-hydrogen.

The spectrum of 2M–TCNE consists of bands λ_1 575, λ_2 455, and λ_3 350 sh nm. The PE bands of 2M at 7.82, 8.69, and 9.92 eV[13] yield calculated λ_{CT} values of 562, 449, and 330 nm. These data predict that β-Me substitution will produce approximately equal increases in λ_1 and λ_2 for 2M–TCNE relative to N–TCNE. Since the observed shifts for both $\Delta\lambda_1$ and $\Delta\lambda_2$ are 25 nm it is reasonable to assume that the CT bands arise from the inductive interactions at of β-Me with a_u and b_{1u}. The spectrum of

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2E–TCNE exhibits bands at λ_1 580 and λ_2 460 nm which are slightly shifted from those observed for 2M–TCNE.

Analysis of the spectra of 1M–, 1E–, and 2M–TCNE yield nearly identical K values of 1.04, 1.10, and 1.07 L/mol and ϵ values of 1420, 1270, and 1520 L/mol-cm. However, the Scott graph for a system with excess 2M exhibits strong curvature, indicating the presence of D_2T species. The graph for a system with excess TCNE yields ϵ 573 L/mol-cm and a surprisingly large value for K of 2.90 L/mol.

The spectrum of 2V–TCNE with bands λ_1 580 and λ_2 465 nm has wavelength shifts $\Delta\lambda_1$ and $\Delta\lambda_2$ relative to N–TCNE of 30 and 35 nm which arise from the conjugation of the π_e olefinic orbitals of the vinyl group with a_u and b_{1u}. The I_1 and I_2 values of 7.93 and 8.53 eV[15] for 2V correspond to λ_1 and λ_2 values of 579 and 472 nm.

3. **Dialkylnaphthalenes.** It is convenient to divide complexes of these donors into three classes depending upon the number of α and β substituents on the donor ring.

a. **α,β-Dialkylnaphthalenes.** This class, which includes 12M–, 13M–, and 16M–TCNE, displays bands λ_1 610–616, λ_2 460–463, and λ_3 335–350 sh nm. The $\Delta\lambda_1$ and $\Delta\lambda_2$ shifts relative to N–TCNE are 60–65 and 30–33 nm. These wavelength shifts are rationalized by assuming, on the basis of the data in Table II, that the inductive effects of each of the methyls on the a_u and b_{1u} orbitals are independent and additive. The $\Delta\lambda_1$ shifts for 1M– and 2M–TCNE are 36 and 25 nm; their sum, 61 nm, is practically identical to the $\Delta\lambda_1$ shifts observed for the complexes of the α,β-dimethylnaphthalenes. Accordingly, the $\Delta\lambda_2$ shifts for 1M– and 2M–TCNE are 5 and 25 nm; their sum, 30 nm, is essentially identical to the $\Delta\lambda_2$ shifts observed for the complexes of the α,β-naphthalenes.

The PE spectra of 12M, 13M, and 16M exhibit bands at 7.78 and 8.53 eV,[13] 7.86 and 8.61 eV,[13] and 7.80 and 8.53 eV,[15] which yield λ_1 and λ_2 values of 613 and 472 nm, 594 and 460 nm, and 608 and 472 nm, in good agreement with the observed values of 615 and 460 nm, 613 and 462 nm, and 610 and 463 nm for 12M–, 13M–, and 16M–TCNE.

The K values for 12M–, 13M–, and 16M–TCNE at 1.54, 1.42, and 1.78 L/mol are considerably higher than those of N–TCNE. Since the K values obtained from the analysis of the 13M–TCNE system appear to be fairly constant over a wide range of concentrations it is assumed that only negligible amounts of D_2T species occur in this system.

b. **α_2-Dialkyl- and α_2-Cycloalkenonaphthalenes.** The spectra of 14M–, 15M–, 18M–, and ANT–TCNE, display bands at λ_1 615–655, λ_2 440–442, and λ_3 330–360 sh nm. The $\Delta\lambda_1$ and $\Delta\lambda_2$ shifts relative to N–TCNE are 60–65 and 30–33 nm. These shifts are rationalized by assuming the additivity of the inductive effects of each of the methyls on the a_u and b_{1u} orbitals. The spectrum of the ANL–TCNE system, which exhibits only one band at λ 510 near the ANL cutoff at 450 nm, is treated apart from the other members of the group.

Since the $\Delta\lambda_1$ shift for 1M–TCNE is 36 nm, the expected $\Delta\lambda_1$ shift for the α_2-methylnaphthalenes, assuming additivity of the inductive effect, is 72 nm. The observed $\Delta\lambda_1$ shifts for 14M–, 15M–, 18M–, and ANT–TCNE are 65, 67, 80, and 105 nm, indicating that these λ_1 bands arise from $\pi^* \leftarrow a_u$ transitions. The larger $\Delta\lambda_1$ shifts for 18M– and ANT–TCNE (Table III) are probably due to distortions in the naphthalene ring caused by *peri*-methyl steric interactions (see below).

Since the $\Delta\lambda_2$ shift for 1M–TCNE is 5 nm, the expected $\Delta\lambda_2$ shift for the α_2-methylnaphthalenes is 10 nm. The observed $\Delta\lambda_2$ shifts for 14M–, 15M–, 18M–, and ANT–TCNE (10, 12, 10, and 10 nm) are consistent with expectation.

The PE spectra of 14M and 15M exhibit ionizations at 7.82, 8.69, and 9.54 eV and at 7.85, 8.69, and 9.50 eV,[13] which yield calculated λ_{CT} values of 604, 449, and 360 nm and of 597, 449, and 363 nm for 14M– and 15M–TCNE. The observed values for these complexes are 615, 440, and 320 sh nm and 617, 442, and 352 nm. The PE spectrum of 18M[13] exhibits ionization bands at 7.64, 8.60, and 9.52 eV which yield λ_{CT} values of 636, 462, and 361 nm for 18M–TCNE which are comparable with the observed values of 630, 440, and 360 sh nm. Structurally related ANT has ionizations at 7.76, 8.68, and 9.65 eV[13] which yield calculated λ_{CT} values of 618, 451, and 351 nm for ANT–TCNE; the observed values are 651, 443, and 335 nm.

We note that the I_1 values of 14M and 15M are nearly identical at 7.82 and 7.85 eV, whereas the I_1 value of 18M is somewhat lower at 7.64 eV. Studies of the PE spectra of 1,5- and 1,8-diaminonaphthalenes by Maier[16] suggest that this difference is due to steric interactions between the *peri*-methyls. The structurally related compounds 18M and ANT are known to have severe angular distortions in the ring relative to N due to the Me–Me repulsions in the case of 18M[17] and to the squeezing of the 8_a–1_a distance in the case of ANT.[18] The skeletal structure of 15M,[19] on the other hand, is nearly identical to that of N.

The K values of 14M–, 15M–, 18M–, and ANT–TCNE at $C_D/C_T = 1/10$ are 2.52, 0.83, 1.15, and 2.34 L/mol. Since the K values obtained from the analysis of the 14M–TCNE and ANT–TCNE systems appear to have much larger values in excess TCNE than in excess donor it is assumed that appreciable amounts of D_2T species occur in these systems.

The spectrum of the ANL–TCNE system is unique among the naphthalene/TCNE systems investigated in this study. ANL itself is a red-brown solid which absorbs strongly at $\lambda < 470$ nm. The spectrum of the ANL–TCNE system consists of a very broad band with λ_{max} 505 nm which abuts the cutoff. Consequently half of the absorbance band of the complex is obscured. When the absorbance due to the donor is subtracted from the gross spectrum a corrected band for the complex emerges which has a $\Delta\nu_{1/2}$ value of about 9100 cm^{-1}. Since this width is nearly double that of a normal CT band, it is apparent that the complex band arises from two or more electronic transitions. The PE spectrum reported by Boschi et al.[20] exhibits ionization bands at 8.22, 8.39, and 8.99 eV which correspond to CT transitions at 521, 493, and 413 nm. The first two of the calculated bands are only 28 nm apart; consequently they would be expected to overlap strongly to yield a broad composite band with λ_{max} 505–510 nm which in fact is observed. The K value of 1.30 L/mol obtained for this system is in the normal range for TCNE complexes of α_2-methylnaphthalenes.

The λ_1 and λ_2 values of 626 and 445 nm for 14B–TCNE reported by Evans et al.[14] again show larger $\Delta\lambda_{CT}$ shifts (Table III) than corresponding shifts for 14M–TCNE, indicating that an α-*t*-Bu group produces a larger inductive effect on the naphthalene ring than an α-Me or that there

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is a steric interaction between the *t*-Bu and the *peri*-hydrogen which produces a distortion of the ring. Note that the combined $\Delta\lambda_{CT}$ shifts for 14B–TCNE are about double those for 1B–TCNE.

c. β_2-Dialkylnaphthalenes. The spectra of 23M–, 26M–, and 27M–TCNE exhibit bands λ_1 and λ_2 at 595–600, 475–492, and 320–350 sh nm. The $\Delta\lambda_1$ and $\Delta\lambda_2$ shifts with respect to N–TCNE at 45–50 and 45–62 nm are approximately double the corresponding shifts for 2M–TCNE, indicating that the inductive effect of the β-Me is additive.

The PE spectrum of 23M displays bands at 7.89, 8.52, and 9.79 eV,[13] which yield λ_{CT} values of 587, 473, and 340 nm for 23M–TCNE; the PE spectrum of 26M has bands at 7.78, 8.50, and 9.70 eV,[15] which yield λ_{CT} values of 613, 476, and 347 nm for 26M–TCNE; and the PE spectrum of 27M has bands at 7.83, 8.44, and 9.73 eV,[15] which correspond to λ_{CT} 601, 485, and 344 nm. These values are in good agreement with the experimental results. The *K* values of 23M–, 26M–, and 27M–TCNE at 1.46, 2.73, and 1.94 L/mol are in the normal range for dimethylnaphthalene–TCNE complexes.

Evans et al.[14] reported λ_1 and λ_2 values of 620 and 487 and 610 and 501 nm for 26B- and 27B-TCNE. Both the $\Delta\lambda_1$ and $\Delta\lambda_2$ shifts average out to 32 nm per *t*-Bu, again slightly larger than comparable shifts for 26M- and 27M–TCNE. Since there is no possibility of steric peri interactions in 26B and 27B, the $\Delta\lambda$ shifts must be due entirely to inductive effects. The exceptionally low *K* value for 26B–TCNE at 0.63 L/mol is undoubtedly due to bulky *t*-Bu groups which hinder effective intermolecular contact between the donor and acceptor.

d. Summary. The λ_1 and λ_2 values for TCNE complexes of N and its mono- and dimethyl derivatives are given in Table III. Wavelength shifts relative to N–TCNE, $\Delta\lambda_1$ and $\Delta\lambda_2$, which arise from the inductive effect of unhindered methyl and *t*-Bu substituents, are calculated and averaged. The results show that an unhindered α-Me independently produces mean shifts of 36 and 5 nm on λ_1 and λ_2 whereas an unhindered β-Me produces mean shifts of 25 and 27 nm on λ_1 and λ_2. Values of λ_1 and λ_2 for TCNE complexes of polymethylnaphthalenes can be estimated by using the empirical equations

$$\lambda_1 = 550 + 36n_\alpha + 25n_\beta \tag{3}$$

$$\lambda_2 = 430 + 5n_\alpha + 27n_\beta \tag{4}$$

where n_α and n_β are the number of α- and β-methyls. These equations are not valid for systems in which the naphthalene skeleton is appreciably distorted by steric interactions between substituent groups. The difference between the coefficients of n_α and n_β arises from the fact that the electron density of the HOMO is greater on the α than on the β carbon. We note that although the $\Delta\lambda_1$ and $\Delta\lambda_2$ shifts for a β-Me are nearly equal, the corresponding CT energy shift, $\Delta h\nu_1$, is somewhat larger than $\Delta h\nu_2$.

Although the λ_1 and λ_2 values of only four *t*-Bu derivatives have been published, the data suggest that reasonable predictions can be made for λ_{CT} values for TCNE complexes of *tert*-butylnaphthalenes by replacing the parameters in eqs 3 and 4 with the values 40 and 32 and 8 and 32.

4. Polyalkylnaphthalenes. The spectrum of 235M–TCNE exhibits bands at λ_1 630, λ_2 495, and λ_3 345 nm. The absorbance bands calculated for this complex of an α,β_2-trimethylnaphthalene from eqs 3 and 4 are λ_1 636 nm and λ_2 485 nm. The calculated values are in excellent agreement with experiment, indicating that inductive effects of the methyl groups are additive in this case of a structurally unstrained naphthalene. The I_1 and I_2 values of 7.68 and 8.32 eV[16] correspond to λ_1 639 and λ_2 504 nm.

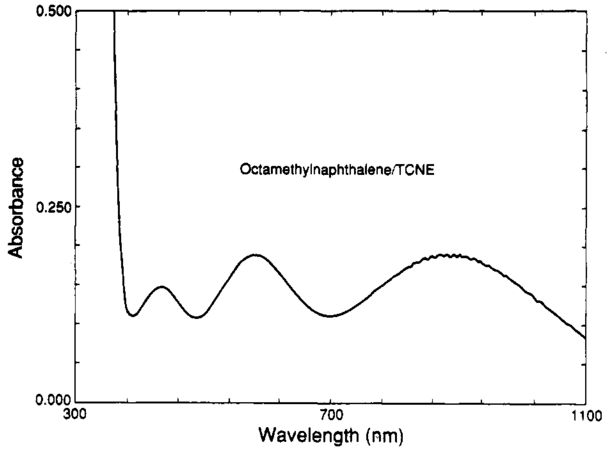

Figure 3. Spectrum of octamethylnaphthalene–TCNE.

The spectrum of HHP–TCNE displays bands at λ_1 751, λ_2 460, and λ_3 405 nm. The structure of HHP is akin to an α_4- or 1,4,5,8-tetramethylnaphthalene in which each pair of *peri*-methyls is joined by a –CH$_2$– bridge bent back at an angle perpendicular to the plane of the ring. The values calculated with eqs 3 and 4 at λ_1 694 and λ_2 450 nm are 60 and 10 nm lower than the observed values suggesting that the HHP ring is severely strained. The I_D values of 7.33, 8.43, and 9.03 eV[16] correspond to λ_1 748, λ_2 487, and λ_3 409 nm, in good agreement with observation.

Solutions of HXM and TCNE exhibit abnormally weak bands at λ_1 795, λ_2 490 sh, and λ_3 415 sh, indicating the presence of HXM–TCNE. The value calculated by eq 2 at λ_1 744 nm is 41 nm lower than the observed value expected for a ring strained by the presence of two *peri*-methyl groupings. The PE spectrum exhibits ionizations at 7.42, 8.26, and 8.96 eV,[15] which correspond to λ_{CT} values of 717, 514, and 416 nm. The extremely low absorbance of the complex precludes the possibility of calculating ϵ and *K* values.

The spectrum of HPM–TCNE exhibits bands λ_1 772, λ_2 565, and λ_3 400 nm. The values calculated by eqs 3 and 4 at λ_1 758 nm and λ_2 549 nm are 14 and 16 nm less than the observed values as expected for a molecule with a pair of *peri*-methyl groups. The I_D values of 7.17, 7.84, and 8.75 eV[15] correspond to λ_1 838, λ_2 599, and λ_3 442 nm which are in poor agreement with observation. Analysis of the data yields a *K* value of 60.2 L/mol. The highest *K* value previously reported for a TCNE complex of a hydrocarbon is that for hexamethylbenzene–TCNE at 20.74 L/mol.[10]

Hart and Oku[21] observed that TCNE produces a deep blue color with OCM in benzene, chloroform, and hexane solutions. We found that OCM–TCNE exhibits bands at λ_1 885, λ_2 582, and λ_3 438 nm (Figure 3). The values calculated by eqs 3 and 4 for the α_4,β_4-OCM–TCNE complex, λ_1 794 and λ_2 550 nm, are 91 and 32 nm lower than the experimental values. Structural studies[22] show that the ring is strongly distorted by steric Me–Me interactions; consequently wavelength shift calculations should yield low values as observed. The PE spectrum displays ionizations at 6.98, 7.73, and 8.49 eV,[15] which correspond to λ_{CT} values of 903, 626, and 478 nm; all of these values are 20–40 nm higher than the observed values. A value of 40.8 L/mol was obtained for *K*.

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5. **Perylene.** Kuroda et al.[4] reported that the spectrum of PRL–TCNE in DCM exhibits maxima at 900 and 870 nm. Dewar and Thompson[23] reported λ_{CT} 915 nm and K 4.03 L/mol in $CHCl_3$. We observed a single smooth band with λ_{CT} 890 nm and $\Delta\nu_{1/2}$ 4100 cm^{-1}. The PE spectrum reported by Boschi et al.[24] exhibits ionizations at 7.00 and 8.55 eV which correspond to λ_{CT} values of 892 and 469 nm. The first value is in excellent agreement with our observed value of 890 nm whereas the band expected to arise from the second ionization is not observed because of the strong absorbance of PRL at 300–500 nm. Our values of ϵ 1440 L/mol-cm and K 3.45 L/mol are similar to those observed in related donor–TCNE systems.

6. **Biphenylenes.** Farnum et al.[25] reported ϵ 500 L/mol-cm, K 5.1 L/mol, and λ_{CT} 680 nm for BPL–TCNE. Subsequently Emslie et al.[26] reported corresponding values of ϵ 3290 L/mol-cm and K 0.71 L/mol. Our values of 3100 L/mol-cm and 0.89 L/mol support Emslie's results. The PE bands at 7.56 and 8.90 eV reported by Eland[27] arise from ionizations from the $3a_2$ (three nodes perpendicular to the long axis) and $2a_2$ (nodes coincident with the two c_2 axes) orbitals.[28] These ionizations ocrrespond to λ_1 and λ_2 values of 670 and 423 nm, which are comparable to our experimental values of λ_1 677 and λ_2 412 sh nm.

Farnum also reported λ_1 values of 715 and 765 nm for 18MB– and 27MB–TCNE which correspond to $\Delta\lambda_1$ shifts of 38 and 88 nm. OMB–TCNE displays bands λ_1 875 and λ_2 560 nm, yielding a $\Delta\lambda_1$ value of 195 nm. These shifts are consistent with expectations based on the symmetries of the two orbitals. The K value of 411 L/mol for OMB–TCNE is the largest yet observed for a CT complex of TCNE with a hydrocarbon.

7. **Azulene.** Kuroda et al.[4] reported a λ_{CT} value of 630 nm for AZL–TCNE in DCM whereas Dewar et al.[23] reported λ_{CT} values of 740 and 735 nm and a K value of 14.60 L/mol in chloroform. The study of this system is complicated by the overlap of the AZL spectrum (λ_{max} 580 nm, ϵ 329 L/mol-cm)[29] with the CT band of AZL–TCNE. We observed that the subtraction of the AZL band from the composite band for the AZL–TCNE system reveals a net CT band with λ_1 and λ_2 values of 686 and 470 sh nm. Analysis of this system yields ϵ 3590 L/mol-cm, K 10.01 L/mol, and $\Delta\nu_{1/2}$ 4700 cm^{-1}. The width of the λ_1 band is characteristic of CT bands. The unusually high K value relative to that for N–TCNE may be due to the strong interaction between TCNE and the five-membered ring of AZL which is reported to bear a negative polarity.[30]

Values of I_1 7.42 and I_2 8.49 eV[8] for the a_2 and b_1 orbitals of AZL correspond to λ_{CT} values of 717 and 477 nm which are midway between our λ_1 values and those reported by Dewar.

8. **Bicycloalkenes.** Frey et al.[10] reported that the spectrum of CHX–TCNE exhibits a band λ_{CT} 415 nm which arises from a $\pi^* \leftarrow \pi_e$ transition. The related bridged cycloalkene, BHP, forms a complex BHP–TCNE with λ_1 430 n. Bischof et al.[31] observed I_1 values for CHX and BHP of 9.12 and 8.97 eV which correspond to λ_1 values of 399 and 415 nm for CHX– and BHP–TCNE. The $\Delta\lambda_1$ shift of 30 nm, observed in BHP–TCNE relative to CHX–TCNE, and the corresponding ΔI_1 shift in BHP and CHX, must be due to strain on the double bond produced by the bridging $-CH_2-$ in BHP since the substitution of an alkyl group on a carbon once-removed from the double bond has only a slight inductive effect.

Similar shifts are observed in the spectra of CHXD– and bridged BHPD–TCNE where λ_1 and λ_2 are 440 and 340 nm and 470 and 385 nm. Bischof et al. report I_1 and I_2 values of 8.80 and 9.80 eV for CHXD and 8.69 and 9.55 eV for BHPD; these values correspond to λ_1 and λ_2 values of 435 and 339 nm for CHXD–TCNE and of 449 and 359 nm for BHPD–TCNE. They attribute the difference between corresponding I_1 and I_2 values in these compounds to enhanced "homoconjugation" or "through-space" interaction between the double bonds which are forced into an alignment in which the π_e orbitals overlap. The $\Delta\lambda_1$ shifts of 15 nm and $\Delta\lambda_2$ shift of 20 nm we observed in BHPD–TCNE relative to CHXD–TCNE are attributable to both steric strain and to a "through-space" interaction between the double bonds in BHPD.

Summary and Conclusions

1. **Correlation of λ_{CT} with I_D.** Values of λ_{CT} for TCNE complexes of naphthalene and its alkyl and alkenyl derivatives tend to correlate well with I_D values from PE spectra. Values of λ_{CT} calculated from eq 2 generally fall within ±5% of experimental results.

2. **Effect of Alkyl Substituents on *K*.**

a. K values for TCNE complexes of naphthalenes tend to increase with the degree of alkyl substitution. Some of the highly methylated naphthalenes form complexes with K values more than double the highest values reported heretofore.

b. For most of these D–TCNE systems, K values tend to decrease as C_D/C_T increases indicating the presence of both DT and DT_2 species.

3. **Effect of Alkyl Substituents on λ_{CT}.** Unhindered methyl substituents increase λ_{CT} values through inductive interactions with the π orbitals of the naphthalene ring.

a. Unhindered α-Me substituents increase λ_1 and λ_2 values of TCNE complexes of naphthalenes by mean values of 36 and 25 nm per methyl group relative to N–TCNE; unhindered β-Me substituents increase λ_1 and λ_2 by mean values of 5 and 27 nm per methyl (eqs 3 and 4).

b. α-*t*-Bu substituents increase λ_1 and λ_2 values of TCNE complexes of naphthalenes by about 40 and 33 nm relative to N–TCNE, whereas β-*t*-Bu substituents increase λ_1 and λ_2 by mean values of 8 and 32 nm.

c. *peri*-Alkyl substituents produce distortions in the naphthalene ring which result in abnormal shifts in λ_1 and λ_2.

Acknowledgment. We are grateful for financial support from the Faculty Research Grant Fund and the Office of the Vice-President for Academic Affairs of Northern Michigan University. We thank Dr. Rolf Gleiter of the Organisch-Chemisches Institut of Heidelberg University for providing PE spectra of several compounds and for his hospitality and assistance during the preparation of this paper. We are grateful to Dr. Harold Hart of Michigan State University for the gift of several valuable polymethylnaphthalenes.

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