Electronic Effects of Cyanocarbon Groups

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Abstract: The electronic properties of β,β-dicyano- and α,β,β-tricyanovinyl groups have been determined from pK_a measurements on substituted N,N-dimethylanilines and from F^{19} nmr chemical shifts on fluorobenzenes. The tricyanovinyl group is much more strongly electron withdrawing by both resonance and inductive mechanisms than a nitro group, and the β,β-dicyanovinyl group is comparable to a nitro group. Solvent effects on the F^{19} nmr chemical shifts were measured to determine the extent of complexing and interaction. Small variations were observed, but a strong π base had no significant effect on the F^{19} chemical shift, supporting current views that no ionization is involved in π complexing. The results are discussed in terms of current theories on the origin and transmission of electronic effects, particularly in comparison of percyano substituents to other strong electron-withdrawing groups.

The cyano group is recognized as a powerful electron-withdrawing substituent, grossly similar to the nitro group, with a stong inductive influence that can be considerably enhanced by resonance interactions. The cyano group has a cylindrical shape with a strong dipole oriented with the negative end toward nitrogen. In contrast, the nitro group is triangular with the negative charge on the two oxygens revolving to spread the effective negative charge over a large hemispherical area. The relatively low steric requirement of the cyano group compared to nitro is probably a major reason why the unique series of stable percyano aliphatic and aromatic compounds can be prepared.[1] An accumulation of the strongly electron-withdrawing cyano groups leads to molecules with unusual properties, both physical and chemical.[1] Quantitative measurements on the electronic properties of groups multiply substituted with cyano groups are of value not only to gain a better understanding of the properties of cyanocarbons but also to approach the fundamental questions of molecular interactions and mechanism of transmission of electronic effects. Recently the tricyanomethyl group[2] was reported to have unusual electronic properties of significance in understanding the mechanism of electronic transmissions, and further studies of its properties were carried out in conjunction with the present work. Quantitative measurements of the electronic effects of cyano substitutions in cyclopentadienides have also been reported from this laboratory.[3]

Experimental Section

A. **Synthesis.** 1. **Benzylidenemalononitriles** (β,β-dicyanovinylbenzenes) were prepared as described in the literature.[4] The yields and physical and analytical data on all new benzylidenemalononitriles are given in Table I.

2. **Tricyanovinylbenzenes.** The known[4] procedure of hydrogen cyanide addition to benzylidenemalononitrile (from potassium cyanide in aqueous ethanol) and oxidation of the resulting adduct with lead tetraacetate in acetic acid was used; however a modified oxidation procedure using bromine in pyridine[5] gave better yields in some cases. In the modified procedure, 2.91 g (0.13 mole) of *m*-(α,β,β-tricyanoethyl)-N,N-dimethylaniline (isolated as an oil by dichloromethane extraction, prepared from 3.94 g of *m*-(N,N-dimethylamino)benzylidenemalononitrile and 2.6 g of potassium cyanide in 40 ml of 50% aqueous ethanol) was dissolved in 15 ml of pyridine. The pyridine solution was cooled in an ice bath, and, with stirring, 2.3 g (0.14 mole) of bromine in 15 ml of trichlorofluoromethane was added dropwise. After stirring for 15 min at room temperature, the reaction mixture was poured into ice water and filtered. The crude *m*-(tricyanovinyl)-N,N-dimethylaniline, as 2.8 g (98%) of purple solid, mp 125–127°, was recrystallized from benzene–hexane, mp 133.5–135°.

m-(Tricyanovinyl)aniline could not be obtained by either oxidation procedure. The yields and physical and analytical data on all new tricyanovinylbenzenes are given in Table I.

B. **Ionization Constant Measurements.** The procedures described previously[6] were used to determine the ionization constants of anilines in water and N,N-dimethylanilines in dioxane–water (45:55) at 25°. Ionization constant data and calculated σ values are summarized in Table II. *m*-(β,β-Dicyanovinyl)aniline was not sufficiently stable to measure ionization constants under the standard conditions. The *p*-anilinium ions were too acidic to use the normal buffer system, and the ionization constants were determined by extrapolation of $[H^+]$ from a series of measurements at different acidities. This procedure could lead to large errors, but the σ parameters determined for the two different *para*-substituted anilines were in reasonable agreement.

C. **Nmr Calibration.** The F^{19} nmr calibrations were carried out by literature procedures[6,7] on a Varian A-56 nmr using 5% concentrations of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal standard in a series of solvents (fluorotrichloromethane could not be used because fluoroaromatics were not sufficiently soluble). Measurements were made at three concentrations (20, 10, and 5%), and the chemical shifts (Table III) were obtained by extrapolation to infinite dilution.

D. **Substituent Parameters.** The Hammett σ constants were calculated by standard methods[8] from the ionization constant data. Substituent constants were calculated from the F^{19} nmr chemical shift data by the procedure described by Taft and co-workers.[6,7] The σ_I and σ_R or σ_{R^0} parameters were calculated according to Taft.[9] The substituent parameters are listed in Table IV with comparative values for other substituents.

E. **π-Complexing Studies.** Measurements of changes in F^{19} chemical shifts caused by π complexing of the cyanocarbon group required a π base that could be used at very high concentration since a relatively high concentration of fluoroaromatic, compared to that used in the ultraviolet measurement, was required

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[1] For reviews of cyanocarbon chemistry, see T. L. Cairns and B. C. McKusick, *Angew. Chem.*, 73, 520 (1961); B. C. McKusick, *Trans. N. Y. Acad. Sci., Ser. II*, 27, 719 (1965).

[2] J. K. Williams, E. L. Martin, and W. A. Sheppard, *J. Org. Chem.*, 31, 919 (1966).

[3] O. W. Webster, *J. Am. Chem. Soc.*, 88, 3046, 4055 (1966).

[4] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *ibid.*, 80, 2806 (1958).

[5] We are indebted to Dr. W. J. Linn of this laboratory for suggesting this procedure.

[6] W. A. Sheppard, *J. Am. Chem. Soc.*, 87, 2410 (1965).

[7] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, 85, 709, 3146 (1963).

[8] H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

[9] R. W. Taft, *J. Phys. Chem.*, 64, 1805 (1960).

Table I. Di- and Tricyanovinylbenzene Derivatives: Preparation and Properties

Substituents in XC_6H_4R X	R	Mp, °C	Recrystallization Solvent	Prepn (% yield)[a]	Ultraviolet[b] λ_{max}, mμ	ϵ_{max}	Formula	Carbon, % Calcd	Found	Hydrogen, % Calcd	Found	Nitrogen, % Calcd	Found	Fluorine, % Calcd	Found
$CH{=}C(CN)_2$	*m*-NH_2	116–117.5	Ethanol or benzene	A (53)	236 270 314 407	9,940 11,400 18,900 2,300	$C_{10}H_7N_3$	71.0	70.9	4.18	4.25	24.8	24.9		
$CH{=}C(CN)_2$	*m*-$N(CH_3)_2$	128.5–129	Benzene	A (46)	248 282 316 444	10,700 17,200 19,000 2,020	$C_{12}H_{11}N_3$	73.1	72.8	5.62	5.42	21.3	21.5		
$CH{=}C(CN)_2$	*m*-F	89.3–90.1	Carbon tetrachloride or ethanol	A (33)	221 298	6,480 17,000	$C_{10}H_5FN_2$	69.8	69.4	2.93	3.22	16.3	16.5	11.0	10.3
$CH{=}C(CN)_2$	*p*-F	128–129	Carbon tetrachloride	A (61)	228 234 310 432 505	10,000 9,100 53,300 110 10	$C_{10}H_5FN_2$	69.8	69.5	2.93	3.04	16.3	16.2	11.0	10.8
$C{=}C(CN)_2$ CN	*m*-$N(CH_3)_2$	133.5–135	Benzene–hexane	B2 (98)	256 294 345 537	16,300 10,200 12,900 1,320	$C_{13}H_{10}N_4$	70.3	70.3	4.54	4.61	25.2	25.2		
$C{=}C(CN_2)$ CN	*m*-F	97.5–98.5	Xylene or carbon tetrachloride	B1 (39)	241 321	6,380 11,900	$C_{11}H_4FN_3$	67.1	66.9	2.05	2.22	21.3	21.1		
$C{=}C(CN)_2$ CN	*p*-F	122–123[c]	Ethanol, benzene–cyclohexane, or carbon tetrachloride	B1 (39) B2 (31)	244 340	8,080 1,400	$C_{11}H_4FN_3$	67.1	67.2	2.05	2.20	21.3	21.0	9.64	9.65

[a] See Experimental Section for general description of procedures; A, condensation of benzaldehyde with malononitrile; B, addition of HCN to benzylidenemalononitrile followed by oxidation with (1) lead tetraacetate or (2) bromine in pyridine. [b] Solvent ethanol. [c] Prepared first by tricyanovinylation of fluorobenzene: R. Henderson and W. A. Sheppard, *J. Org. Chem.*, 32, 858 (1967).

Table II. Ionization Constants and Substituent Parameters

Water, 25°, $XC_6H_4N^+H_3 \rightleftharpoons XC_6H_4NH_2 + H^+$

X of $XC_6H_4NH_2$		λ_{max}	$-\log K$	σ
H		231	4.56[a]	0
$CH{=}C(CN)_2$	*para*	402	1.29	1.19
$C{=}C(CN)_2$ CN	*para*	488	0.10 ± 0.05[b]	1.62

Dioxane–Water (45:55), 25°

$XC_6H_4N^+H(CH_3)_2 \rightleftharpoons XC_6H_4N(CH_3)_2 + H^+$

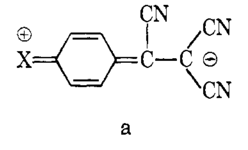
X of $XC_6H_4N(CH_3)_2$				
H		252	4.14 (4.00)[c]	0
$CH{=}C(CN)_2$	*meta*	447	1.76	0.55
	para	442	−0.85	1.20
$C{=}C(CN)_2$	*meta*	570	0.87	0.77
CN	*para*	535	-2.85 ± 0.10[b]	1.70

[a] For calculation of σ values: $\rho = +2.767$.[8] [b] Too acidic for normal buffers; extrapolated value determined from plot of $-\log K$ *vs.* $[H^+]$. [c] For calculation of σ values: $\log K_0 = -4.00$ and $\rho = +4.053$.[6]

to calibrate the F^{19} signal. The π-complexing abilities of several tricyanovinylbenzenes were measured by the method of Merrifield and Phillips.[10] Because of solubility problems, the only practical π base was N,N-dimethyl-*p*-toluidine which could be used as the solvent, thus giving the very high concentrations needed for maximum π complexing. The extent of π complexing at the 5% concentration needed for nmr measurements was calculated from the equation[10] determined at very low concentration by ultraviolet measurements. Since this calculation requires an extended extrapolation which could introduce large errors, the extent of complexing was confirmed by ultraviolet measurements in very thin cells on the solution used for nmr measurements. The π-complexed solution was an intense deep blue, and no decomposition of the π complex during the measurements was detected (the π complex between tetracyanoethylene and N,N-dimethyl-*p*-toluidine was not sufficiently stable to measure) (see Tables V–VII).

Results and Discussion

A quantitative picture of the electronic properties of selected cyanocarbon groups is gained from comparison of the substituent parameters in Table IV. The tricyanovinyl group withdraws electrons much more strongly than nitro from both the *meta* and *para* positions (larger σ_m and σ_p values); its over-all effect is almost as strong as that of the SO_2CF_3 group (which is reported to be the strongest neutral electron-withdrawing group known).[11] The relative extent to which resonance interactions and inductive effects contribute to the over-all electron withdrawal is estimated from the inductive and resonance parameters, σ_I and σ_R.[9] The inductive effect is enhanced slightly, but most of the increase in electron-withdrawing power of the tricyanovinyl group over cyano or nitro appears to come from very large resonance interactions. A major contribution by a dipole-separated resonance form a is expected because the negative charge is strongly stabilized by the two cyano groups α to the negative charge (hydrocyanocarbons are highly acidic and sometimes can only be isolated as an anion).[12] The β,β-dicyanovinyl group is also strongly electron withdrawing; it does not appear to be as strong inductively as a nitro but again shows strong resonance interaction. The tricyanovinyl group shows an enhanced resonance



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(10) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, 80, 2778 (1958).

(11) W. A. Sheppard, *ibid.*, 85, 1314 (1963).

(12) R. H. Boyd, *J. Phys. Chem.*, 67, 737 (1963).

Table III. F^{19} Chemical Shifts for Fluorobenzenes (XC_6H_4F) at Infinite Dilution Relative to Fluorobenzene

Substituent X of XC_6H_4F		$-\delta$ in solvents,[a] ppm					
		CCl_3F	Benzene	Dioxane	Acetonitrile	Acetone	Methanol
CN	*meta*	2.69 (2.75)[c]	2.75[b]	2.30[b]	2.68[b]	2.75[b]	3.10[b]
	para	9.07 (9.20)[c]	9.05[b]	8.95[b]	9.90[b]	9.70[b]	10.25[b]
$C(CN)_3$	*meta*	−6.46[d]	6.33[e]	4.67	5.04	4.94	5.38
	para	−6.71[d]	5.80[e]	4.81	5.80	5.53	5.84
$CH{=}C(CN)_2$	*meta*	. . .	2.27	2.16	2.37	2.25	2.56
	para	. . .	10.93	10.32	10.95	10.86	11.25
$C{=}C(CN)_2$ | CN	*meta*	. . .	4.12	3.65	3.62	3.41	3.80
	para	. . .	13.19	11.86	12.71	12.10	12.48
NO_2	*meta*	3.45[c]	3.25[b]	2.78[b]	3.33[b]	3.40[b]	3.60[b]
	para	9.55[c]	9.45[b]	9.10[b]	10.35[b]	10.10[b]	10.35[b]

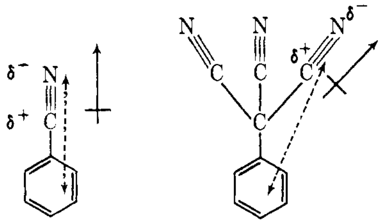
[a] With exception of CCl_3F or CCl_4, calibrations were run in solvent containing 5% 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal calibrant. Chemical shifts (in cps) of fluorobenzene at infinite dilution in each solvent relative to internal standard are: benzene −34, dioxane −16, acetonitrile +31, acetone +15, methanol +11, and fluorotrichloromethane +6282. [b] Values from ref 7. [c] Values in CCl_4 from ref 7. [d] Reference 2. [e] Values reproducible within 0.02 ppm.

Table IV. Substituent Parameters

Group	Method[a]	σ_m	σ_p	σ_I	σ_R
CN	A[b]	0.65	1.02	0.53	0.41
	F[c]	0.58	0.69	0.47	0.22
$CH{=}C(CN)_2$	A	0.55	1.20	0.43	0.75
	F	0.45	0.70	0.41	0.29
$C{=}C(CN)_2$ | CN	A	0.77	1.70	0.60	1.08
	F	0.83	0.98	0.67	0.31
NO_2	A[d]	0.70	1.17	0.55	0.61
	F[c]	0.67	0.77	0.57	0.20
$C(CN)_3$	F[e]	0.97	0.96	0.98	−0.02
$CH{=}CH_2$	F[c]	0	−0.02	0.01	−0.03
SO_2CF_3	A[f]	1.00	1.65	0.84	0.73
	F[g]	0.90	1.06	0.75	0.31

[a] Method F, from F^{19} chemical shift measurements in benzene; A, from pK_a of anilinium or N,N-dimethylanilinium ions. [b] Values from M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Am. Chem. Soc.*, **81**, 4228 (1959). [c] Reference 7. [d] Reference 6. [e] Reference 2. [f] Reference 11. [g] Private communication from Professor R. W. Taft.

effect over the dicyanovinyl which is difficult to explain by a classical resonance picture. Apparently the α-cyano group interacts with the π-ethylenic system by an inductive mechanism or through orbital overlap to provide an additional stabilization for form a. The stabilizing effect of cyano groups on quinomethans (*e.g.*, tetracyanoquinodimethan)[13] may be related to this enhancement of the resonance effect. The cyano groups have a very large effect on the electronic properties of the vinyl group (also note properties of tetracyanoethylene) which is essentially electronically neutral when unsubstituted, and these effects are transmitted very well over a large distance to the aromatic ring. One important factor that emerges from these data is that the field effect or through-space interactions[14] are very important for these highly polarized groups. A clearer demonstration of this field effect is evident in the tricyanomethyl group.[2] This group, as expected, shows essentially zero resonance effect but has a much larger inductive effect (σ_I = 0.98) than would be predicted from the inductive effect of a cyano (σ_I = 0.47). If the normal fall-off factor of one-third is used, the $C(CN)_3$ should have the same σ_I value of 0.47 as does cyano. Through-space interaction (field effect) is the most reasonable explanation for this enhanced inductive effect; in the tricyanovinyl group, the dipoles of the cyano groups on the tetrahedral carbon are oriented in a different direction and should have more through-space effect than a cyano directly on the aromatic ring. This view is supported by abnormal solvent effects on chemical shifts for tricyanomethyl and tricyanovinyl groups. Normally, more polar solvents such as acetonitrile or hydrogen-bonding solvents like methanol enhance the downfield shifts of strong neutral electron-withdrawing groups (note nitro and cyano in Table III), but for tricyanomethyl and tricyanovinyl groups, the largest downfield shifts are for the less polar solvents. In methanol or acetonitrile, the shift is upfield relative to benzene or $CFCl_3$. A dampening of transmittal of through-space effect by hydrogen bonding or dipole–dipole interactions must occur.[15] If the transmittal of charge effect were mainly through the molecule, then interaction with polar solvents, particularly on the negative end of the dipole on nitrogen, should enhance the electron-withdrawing effects.



Dr. R. W. Taft suggested[16] that the enhanced inductive effect could be related to the high stability of the tricyanomethide ion, which would greatly increase the polarization of the carbon–carbon bond between the tricyanomethyl group and the ring. But again the solvent effects are reverse to what is expected for stabilization of the dipolar form.

The resonance effect for the tricyanomethyl group varies from small negative to positive values depending on the solvent used for the F^{19} chemical shift measure-

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(13) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

(14) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3548 (1962), and M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966), have recently interpreted experimental evidence that the so-called "inductive effect" of classical organic theory is a direct field effect, acting across space rather than by successive polarization of intervening bonds and that "inductive" type substituents such as CF_3 operate mainly by a field effect.

(15) For a discussion of solvent interactions, see (a) R. W. Taft, G. B. Klingensmith, and S. Ehrenson, *ibid.*, **87**, 3620 (1965); (b) C. D. Ritchie and A. L. Pratt, *ibid.*, **86**, 1571 (1964).

(16) Private communication.

Table V. π Complexes Formed between Cyanoolefins and π Bases

Cyanoolefins	π base	Solvt	*K*	λ_{max}, A	ϵ, l. mole^{-1} cm^{-1}
$(NC)_2C{=}C(CN)_2$[a]	Hexamethylbenzene	CH_2Cl_2	263	5450	4390
$(NC)_2C{=}C(CN)C_6H_5$	Hexamethylbenzene	CH_2Cl_2	12.6	4400	1600
$(NC)_2C{=}C(CN)(m\text{-}FC_6H_4)$	Hexamethylbenzene	CH_2Cl_2	10	4450	2200
$(NC)_2C{=}C(CN)(p\text{-}FC_6H_4)$	Hexamethylbenzene	CH_2Cl_2	12	4550	1800
$(NC)_2C{=}C(CN)_2$[a]	Durene	CH_2Cl_2	54.2	4800	2075
$(NC)_2C{=}C(CN)C_6H_5$	Durene	CH_2Cl_2	8.9	4300	830
$(NC)_2C{=}C(CN)_2$[a]	Pyrene	CH_2Cl_2	29.5	7240	1137
$(NC)_2C{=}C(CN)C_6H_5$	Pyrene	CH_2Cl_2	6.4	5100	1000
$(NC)_2C{=}C(CN)_2$	Dioxane	CH_2Cl_2	2.3	3520–3580	1950
$(NC)_2C{=}C(CN)C_6H_5$	Dioxane	CH_2Cl_2	*b*	...	...
$(NC)_2C{=}C(CN)C_6H_5$	N,N-Dimethyl-*p*-toluidine (DMT)	CH_3CN	7.7	5650	290
$(NC)_2C{=}C(CN)(m\text{-}FC_6H_4)$	DMT	CH_3CN	8.0	5700	650–800
$(NC)_2C{=}C(CN)(p\text{-}FC_6H_4)$	DMT	CH_3CN	4–8	5900	700–1200

[a] Values from ref 10. [b] Complex too weak to observe even with 50% dioxane.

Table VI. Complexing of Fluoro(tricyanovinyl)benzenes Measured at 5% Concentration in 0.1-mm Cell

$XC_6H_4C(CN){=}C(CN)_2$	Solvt syst (%)	Opt den	Est % complexed
m-F	$DMT\text{-}CCl_3F$ (98:2)	3.91	240
p-F		3.45	100–200
m-F	$DMT\text{-}CH_3CN\text{-}CCl_3F$ (50:48:2)	1.93	120
p-F		2.12	80–120
m-F	$DMT\text{-}CH_3CN\text{-}CCl_3F$ (25:73:2)	1.08	60
p-F		1.23	40–80

Table VII. Effect of π Complexing with N,N-Dimethyl-*p*-toluidine (DMT) on F^{19} Chemical Shifts

System (%)	Est % π complexed	$-\delta$ of $FC_6H_4C(CN){=}C(CN)_2$ relative to C_6H_5F,[a] ppm *meta*	*para*
$DMT\text{-}CCl_3F$ (98:2)	80–100	3.17	11.96
$DMT\text{-}CH_3CN\text{-}CCl_3F$ (50:48:2)	50–100	3.63	12.81
$DMT\text{-}CH_3CN\text{-}CCl_3F$ (25:73:2)	30–80	3.67	12.87

[a] Chemical shift, δ in cps, of 5% fluorobenzene derivative relative to internal standard (concentration of DMT) = −40 (98), +7 (50), and +20 (25).

ments. This variation must result from specific solvent interactions. The major significance of the negligible resonance effect is that the π-inductive effect, as proposed by Dewar[2,6,17] to explain the +R effect of the trifluoromethyl group, cannot be important. By extrapolation from the σ values for the trifluoromethyl (σ_I = 0.39 and σ_R = 0.10), a σ_R of 0.2–0.3 is expected for the tricyanomethyl group. This result provides strong support for the proposal of p–π fluorine interaction to give a −R *meta* effect in benzotrifluorides and other fluoroalkyl aromatic derivatives.[6]

The extent of charge transfer in π complexes is a question of interest;[18] the current opinions, based on both experimental and theoretical data, are that charge transfer is negligible in π complexes, particularly of aromatic π bases with cyanocarbons.[18a] Frontier orbitals are very important in providing the configurations that contribute the greatest weight to the most stable charge-transfer state and, although charge-transfer complexing has long been thought to involve ionization, all accumulated evidence shows that an actual ionization process is not involved.

The F^{19} chemical shifts in fluoro(tricyanovinyl)benzenes are a good probe to determine changes in electron density in the π acid as a result of π complexing, particularly since the F^{19} shift is very sensitive to changes in the π system.[7] Any ionization in complexing should cause a large shift upfield relative to uncomplexed form. Unfortunately a major experimental problem is that the *K* for complexing is determined at low concentration (0.003 *M*) by the ultraviolet method, but for the F^{19} measurements a 5% concentration (about 0.2 *M*) is required. The better aromatic π bases such as hexamethylbenzene or durene are not sufficiently soluble to be used at the high concentrations needed to get appreciable complexing, particularly since the *K*'s for complexing are approximately an order of magnitude less for the aryltricyanoethylenes than for the tetracyanoethylene (see Tables V and VI). N,N-Dimethyl-*p*-toluidine (DMT) was suitable as the π base since it could be used as the solvent and had a *K* comparable to hexamethylbenzene (it is apparently too reactive with TCNE to allow time for spectral measurement but did not appear to react with aryltricyanoethylenes). The extent of complexing was estimated not only for the *K* determined at low concentration but also from optical density measurements on the nmr solution using a very short path ultraviolet cell. Increasing concentrations of DMT in acetonitrile caused the F^{19} chemical shift of the tricyanovinylbenzenes to shift upfield but, even with 98% DMT where the extent of complexing was estimated to be over 80% and probably complete, the shift was only 0.45 ppm for *meta* and 0.75 ppm for *para*, within the range of shifts found for other solvents. (In solvent studies, dioxane gave the highest field chemical shift, with 3.65 for *meta* and 11.86 for *para*, and could also be giving some π complex although too little to measure by the ultraviolet method.) If the estimate of extent of complexing is accurate, then the electronic effects and charge transfer resulting from π complexing

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(17) (a) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 154; (b) M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, 88, 354 (1966).

(18) (a) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, 7, 97 (1966); (b) H. H. Greenwood and R. McWeeny, *Advan. Phys. Org. Chem.*, 4, 73 (1966) (see particularly pp 112–118).

in this system are small in agreement with literature reports and discussions.[18] Solvent interaction can give comparable effects.[15] The *p*-fluorophenyl ring could interact directly with the tricyanovinyl derivative (as a result of the $-$R effect of *p*-fluorine substituent) and could decrease electronic effects resulting from intermolecular interaction of the *p*-tricyanovinyl group with the π base. However, the K values are not significantly lower for the *p*-fluorophenyl, indicating that the *p*-fluoro does not significantly change the extent of complexing and also supporting the view that ionization in the π complex is negligible.

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Singlet and Triplet Nitrenes. II. Carbethoxynitrene Generated from Ethyl Azidoformate

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Abstract: Carbethoxynitrene, made by thermolysis and photolysis of ethyl azidoformate, was added to *cis*- and *trans*-4-methylpent-2-ene, and the dependence of the stereospecificity on olefin concentration was measured. The thermolysis experiments can be quantitatively explained by a scheme used previously to correlate the data of analogous experiments with carbethoxynitrene made by α elimination. This scheme assumes that all the nitrene is generated in the singlet state, and that addition of the singlet to olefin competes with intersystem crossing to triplet nitrene. The former adds stereospecifically, the latter nonstereospecifically. The photolysis data are quantitatively in accord with a scheme in which one-third of the nitrene is produced in the tripletst ate, while two-thirds is generated in the singlet form. The singlet nitrene can be trapped selectively by cyclohexane.

In a recent paper,[3] we have examined the addition of carbethoxynitrene,[4] made by α elimination,[5] to *cis*- and *trans*-4-methylpent-2-ene. We concluded the α-elimination reaction of N-(*p*-nitrobenzenesulfonyloxy)urethan ($Ar{-}SO_2O{-}NH{-}COOEt$) gives exclusively the singlet form of carbethoxynitrene. This then decays to the triplet state at a rate of about $^1/_{30}$ of that of the addition of the singlet to *cis*-4-methylpent-2-ene. Skell's rules for the stereospecificity of the addition of singlet and triplet electron-deficient species to $C{=}C$ double bonds[6] were found to be applicable to our nitrene. The dependence of stereospecificity of addition on olefin concentration was found to be quantitatively in accord with the kinetic scheme in Figure 1. Triplet carbethoxynitrene could be selectively trapped by α-methylstyrene.

In the present paper, we extend our work to the thermolysis and photolysis of ethyl azidoformate. As indicated by the selectivities in C–H insertion reactions, α elimination from $ArSO_2O{-}NH{-}COOEt$ and photolysis and thermolysis of ethyl azidoformate give one and the same carbethoxynitrene.[5,7–10] However, the stereospecificity of addition to the double bond of 4-methylpent-2-enes was markedly lower in azide photolysis than in α-elimination experiments.[11] The purpose of the present paper is to resolve this discrepancy.

Results and Discussion

Thermolysis of Ethyl Azidoformate. Ethyl azidoformate was dissolved in mixtures of *cis*-4-methylpent-2-ene and dichloromethane, and thermolyzed in sealed tubes at 100° for 24 hr. The mixture of *cis*- and *trans*-N-carbethoxy-2-isopropyl-3-methylaziridines was analyzed by calibrated gas chromatography as described previously.[3] Figure 2 gives the fraction of *trans*-aziridine as a function of olefin concentration. The curve closely resembles that obtained with carbethoxynitrene produced by α elimination.

Table I contains the data on which Figure 2 is based. These data were treated in the same manner as in our earlier paper,[3] in order to see whether they are in accord with the kinetic scheme of Figure 1, shown for the specific system we used in Figure 3. As before,[3] [T] stands for the fraction of aziridine-forming reaction that goes through the triplet path ($k_1 \rightarrow k_2 \rightarrow k_4$ in Figure 3), [S] is

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