of $SP(OR)_3$ leads to ^{31}P shift changes of ~20 ppm.[10] As with CF_3CO_2H solutions of **2**, unreacted **3** can be recovered upon evaporation of the solvent. Interestingly, **21**, in which the nitrogen is protonated, apparently forms as the main product when **3** is allowed to react with aqueous $HBF_4/Et_2O/CH_2Cl_2$.[11] The reason for the difference in behavior of **3** in this medium and in TFA is not clear, though it may be related to stabilizing solvation effects of water on the ammonium cation **21**.

In a 1:1 mixture of CD_3CN/CH_2Cl_2, addition of 1 equiv of Et_3OBF_4 to **3** produces a precipitate which redissolves on addition of a second equivalent of ethylating agent. The two peaks at ca. +6 and −8 ppm are assigned to **11** (R = Et) and **19**, respectively. Interesting in this respect is the isolation of **20**.

The upfield shifts in the ^{31}P NMR resonance from **10** to **18**, **11** to **19**, **12** to **13**, **14** to **16**, and **15** to **17** are consistent with the observation on isoelectronic/isostructural $M[P(OR)_3]_x^{n+}$ complexes wherein $\delta(^{31}P)$ moves upfield linearly with increasing positive charge.[12,13] Another possible rationale for the upfield shift with increasing positive charge in the hypervalent TBP phosphorus cations reported here is that the second proton increases the P–N bond order at the expense of the apical P–O bond order, resulting in a more "balanced" TPB configuration for the phosphorus.[14] This polarization process is related to that observed in 10-S-4 and 10-I-3 species possessing varying electronegativity differences in the apical ligands.[15,16] Thus, the upfield progression of the ^{31}P chemical shift from four- to five-coordinate phosphorus may be maximized by balanced bond orders in the apical bonds.

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Registry No. **2**, 10022-55-6; **3**, 60028-25-3; 8-P-4-**10** (R = Me), 76570-87-1; 10-P-5-**10** (R = Me), 81041-54-5; 8-P-4-**10** (R = Et), 76570-89-3; 10-P-5-**10** (R = Et), 81041-56-7; 8-P-4-**11** (R = Me), 76570-91-7; 10-P-5-**11** (R = Me), 81041-58-9; 8-P-4-**11** (R = Et), 76570-93-9; 10-P-5-**11** (R = Et), 81041-60-3; 8-P-4-**14**, 102632-36-0; 10-P-5-**14**, 102632-37-1; 8-P-4-**15**, 102632-39-3; 10-P-5-**15**, 102632-40-6; 8-P-4-**16**, 102632-38-2; 10-P-5-**16**, 102733-94-8; 8-P-4-**17**, 102632-41-7; 10-P-5-**17**, 102733-95-9; 8-P-4-**20**, 102632-34-8; 10-P-5-**20**, 102648-84-0; **21**, 102632-35-9.

(10) Skvortsov, N. K.; Ionin, B. I.; Petrov, A. A. *Z. Obshch. Khim.* **1974**, *44*, 220.
(11) The ^1H NMR spectrum of **21** (see Experimental Section) does not display a clean doublet of triplets (OCH_2) and a triplet (CH_2N) as was observed earlier for the related cation $OP(OCH_2CH_2)_3NMe^+$.[4] Contamination by $(HOCH_2CH_2)_3NH^+$ arising from the hydrolysis of **3** or **21** could explain this observation.
(12) Coskran, K. J.; Bertrand, R. D.; Verkade, J. G. *J. Am. Chem. Soc.* **1967**, *89*, 4535.
(13) Yarbrough, L. W.; Verkade, J. G., unpublished results.
(14) We thank a referee for suggesting this possible explanation.
(15) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.
(16) Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127.

Zwitterionic Tetramethylenes as the Common Intermediates in the Cycloaddition and Polymerization Reactions of *N*-Vinylcarbazole with Electrophilic Tetrasubstituted Ethylenes: A New Explanation for "Charge-Transfer" Initiation

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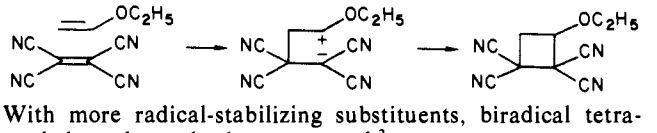
Contribution from the C. S. Marvel Laboratories, Chemistry Department, University of Arizona, Tucson, Arizona 85721. *Received January 7, 1985*

Abstract: The reactions of *N*-vinylcarbazole (NVCZ) with electrophilic tetrasubstituted ethylenes were studied in detail as an example of a reaction whose outcome can be manipulated by changes in concentration, structure, and working procedure to form either small molecules (cyclobutanes, 1-butenes) or poly(vinylcarbazole). Equivalent concentrations and evaporating workup (organic chemists's conditions) lead to small molecules; a large excess of NVCZ and precipitative workup give polymer. The mechanism involves gauche and trans zwitterionic tetramethylenes as intermediates. The former gives cyclobutane reversibly. The latter gives 1-butenes intramolecularly or adds monomers to form cyclohexanes or eventually polymer. The organic chemistry and polymer chemistry is unified on this basis. Extensive stereochemical and kinetics support for these propositions is given. Two other proposed mechanisms for these "charge-transfer" initiations are excluded.

The spontaneous, thermal reaction of electron-rich olefins with electron-poor olefins leads to a rich diversity of both small organic molecules and polymers. The most often encountered small molecules are cyclobutanes. These kinetically favored products isomerize to more thermodynamically favored 1-butene derivatives in more vigorous reaction conditions.

As regards mechanism, organic chemists have proven that tetramethylene intermediates, arising from bond formation between the β-carbons of the reacting olefins, are the keys to small molecules formation. For strongly polar olefins, the penetrating studies of Huisgen[1,2] identified the tetramethylene zwitterion as the intermediate in the cycloaddition reactions, for example,



With more radical-stabilizing substituents, biradical tetramethylenes have also been proposed.[3]

On the polymer side, homopolymers of one or both of the reaction partners or alternating copolymers are formed. To explain these results, Hall recently proposed the Bond-Forming Initiation

(1) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 177.
(2) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.
(3) Bartlett, P. D. *Q. Rev. Chem. Soc.* **1979**, *24*, 473.

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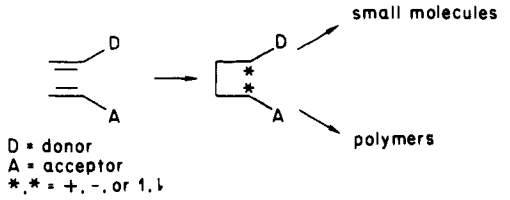
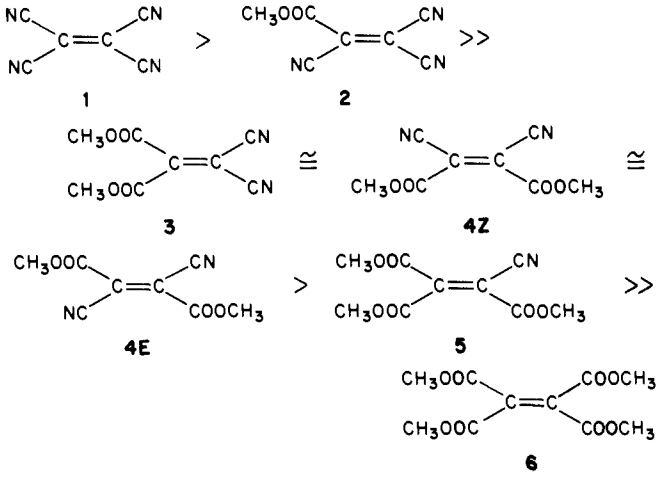
theory, in which the tetramethylene intermediates are proposed as the initiating species for spontaneous polymerization.[4]



Zwitterionic tetramethylenes are postulated to initiate ionic homopolymerizations, while copolymers arise from initiation by biradical tetramethylenes.

Interestingly, the same pairs of reactants have been reported to lead to both small molecules and polymers.[5,6] We postulate that these contrasting results are controlled by the selected experimental conditions: relative concentrations and the mode of workup. "Organic Chemists' Reaction Conditions" using equimolar amounts of both reacting olefins favor the cycloaddition products; "Polymer Chemists' Reaction Conditions", in which one of the reactants is used in excess, favor polymerization. As far as the selected workup is concerned, organic chemists routinely discard "polymeric contaminants", while polymer chemists usually isolate their high molecular weight products by precipitation and filtration with loss of soluble small molecules.

The present study is designed to test the above propositions. We confined our study to strongly polar olefins which would react exclusively via zwitterionic tetramethylene intermediates. As the donor olefin, *N*-vinylcarbazole (NVCZ) was selected; this compound has a great propensity to both cycloadd and polymerize. As electrophiles, seven tetrasubstituted electron-poor olefins, possessing cyano and/or carbomethoxy groups as electron-withdrawing substituents, were chosen: tetracyanoethylene (TCNE) **1**, methyl tricyanoethylenecarboxylate **2**, dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (**3**), dimethyl dicyanomaleate **4Z**, dimethyl dicyanofumarate **4E**, trimethyl cyanoethylenetricarboxylate **5**, tetramethyl ethylenetetracarboxylate **6**.



Both the cycloaddition and polymerization reactions of *N*-vinylcarbazole with the electrophilic olefins have been studied to show that the zwitterionic tetramethylene is the key intermediate in all these reactions and thus prove that the Bond Forming theory is valid for polymerization as well as small molecule formation. The hypothesis that the products are influenced by the reaction conditions has also been tested by running these reactions in both organic chemist's and polymer chemist's conditions.

Results and Discussion

Reaction Partners. On the basis of our results, the reaction scheme in Scheme I is proposed for the reactions of NVCZ in the presence of electrophilic olefins. The gauche and trans tetramethylenes are the key intermediates for both the small molecule formation and the initiation of the homopolymerization of NVCZ.

Each olefin pair can lead to the following small molecules: cyclobutane adducts Cb, 1-butene derivatives Bu, or if the reaction is run in methanol 1-methoxybutanes MeO. In some cases also a 2:1 adduct, namely a cyclohexane derivative, can be formed. In excess NVCZ, its cationic homopolymerization can be initiated. The following system will be followed to number the products: the first digit represents the parent electron-poor olefin and the symbol represents the type of compound, while the letter represents isomers. For example, the cyclobutane adduct of tetracyanoethylene **1** and NVCZ will be represented as compound **1**-Cb, while the methoxybutane obtained from this olefin pair will be represented as compound **1**-MeO.

Electron Deficiency of the Olefins. The observed charge-transfer (CT) absorption maxima for the electron donor–acceptor (EDA) complexes of the electrophilic olefins with different nonreactive electron donors were measured by UV spectroscopy (Table I).[7]

Scheme I

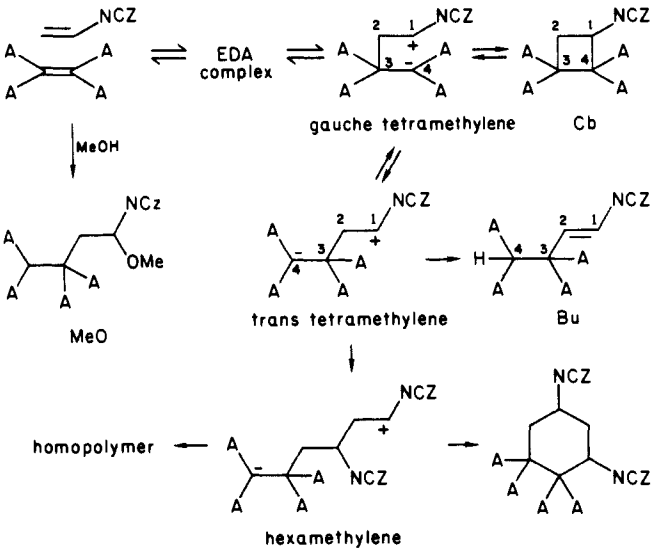


Table I. Observed CT Absoprtion Maxima of EDA Complexes of Electrophilic Olefins with Donors (λ_{max}, nm and 10^{-3} cm^{-1})[a]

	donor					
	N,N-dimethylaniline		*N*-ethylcarbazole		hexamethylbenzene	
olefin	nm	10^{-3} cm^{-1}	nm	10^{-3} cm^{-1}	nm	10^{-3} cm^{-1}
1	680	14.71	588	17.01	537	18.62
2	640	15.63	512	19.53	482	20.75
3	530	18.87	438	22.83	430	23.26
4Z	522	19.16	422	22.63	437	22.88
4E	570	17.54	477	20.96	457	21.88
5	460	21.74	~377	~26.53	~368	~27.17
6	~340	~29.41				

[a] Conditions: at room temperature in chloroform.

Table II. Reduction Potentials of Electrophilic Olefins by Cyclic Voltammetry (E_p, V)[a]

olefin	E_{p1}	E_{p2}
1	−0.15, −0.20[b]	−0.85, −1.06[b]
2	−0.35	−0.30
3	−0.85[b]	*b*
4Z	−0.66	
4E	−0.60[b]	−0.90[b]
5	−0.89	
6	−1.30[b]	−1.80[b]

[a] Conditions: in acetonitrile at room temperature vs. Ag/Ag$^+$. [b] Measured by Cramer.[8]

(4) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(5) Stille, J. K.; Oguni, N.; Chung, D. C.; Tarrin, R. F.; Aoki, S.; Kamachi, M. *J. Macromol. Sci. Chem.* **1975**, *A9*, 745.
(6) Bawn, C. E. H.; Ledwith, A.; Sambhi, M. *Polymer* **1971**, *12*, 209.

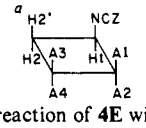
Table III. Cyclobutane Formation from Olefins

olefin	[olefin], M	conditions *a*			EDA color	yield,[b] %	no. of cyclobutane isomers
		solv	temp, °C	time, h			
1	0.63[c]	C_6H_6	26	5	violet	100	1
2	0.30	C_6H_6	26	1	purple	100	4
3	1.0	C_6H_6	26	2	deep red	100	1
4Z	1.0	C_6H_6	26	3	red	100	4
4E	0.025[c]	C_6H_6	80	24	red	100	4
5	1.0	C_6H_6	80	16	orange	100	4
6	0.20[c]	C_6H_6	80	240	yellow	~40	1

[a] 1.1 equiv of NVCZ to electron-poor olefin was used. [b] Yields are based on ^1H NMR measurements after evaporation of solvent. [c] Initially these olefins were not completely soluble but dissolved as the reaction proceeded.

Table IV. ^1H NMR of Cyclobutanes[a]

isomer	substituent				% of tot cyclobutanes	chemical shift δ				coupling const, Hz			solvent
	A1	A2	A3	A4		H1	H2	H2′	CH_3(ester)	$J_{1,2}$	$J_{2,2'}$	$J_{1,2'}$	
1-Cb	CN	CN	CN	CN	100	6.32	4.72	3.83		10.5	14.0	10.0	CD_3CN
2-Cb-a	CN	CN	CN	E	39	6.09	4.84	3.30	3.90	11.8	13.4	9.6	$CDCl_3$
2-Cb-b	CN	CN	E	CN	22	5.98	4.53	3.55	4.11	11.7	13.2	9.7	$CDCl_3$
2-Cb-c	CN	E	CN	CN	31	6.17	4.65	3.40	3.85	~11.6	~13.1	~9.8	$CDCl_3$
2-Cb-d	E	CN	CN	CN	9	~5.96	~4.86	~3.53	3.23	*f*	*f*	*f*	$CDCl_3$
3-Cb	CN	CN	E	E	100	6.06	4.53	3.82	4.00 3.35, 3.46	10.5	13.4	9.0	$CDCl_3$ C_6D_6
4-Cb-a	CN	E	CN	E	39[b] 40[c]	6.23	4.82	3.08	3.85, 4.12	11.5	13.4	10.5	$CDCl_3$
4-Cb-b	CN	E	E	CN	43[b] 28[c]	6.08	4.43	3.31	3.88, 3.98	10.4	13.3	9.7	$CDCl_3$
4-Cb-c	E	CN	E	CN	12[b] 13[c]	6.09	4.64	3.58	3.27, 3.96	11.0	12.5	9.5	$CDCl_3$
4-Cb-d	E	CN	CN	E	7[b] 19[c]	5.98	4.75	3.52	3.07, 3.93	11.9	12.2	9.2	$CDCl_3$
5-Cb	*d*				100	6.0~6.2	4.5~4.7	2.75~3.35	2.53, 3.33, 3.43[e]	~11	~12	~10	C_6D_6
6-Cb	E	E	E	E	100	6.11	4.54	2.81	2.99, 3.81, 3.85, 3.94	11.8	12.6	9.8	$CDCl_3$

[a] 

E = $-COOCH_3$. Absorptions due to aromatic ring protons are not listed here. They fall in the range of 7.00–8.20 ppm. [b] From reaction of **4E** with NVCZ. [c] From reaction of **4Z** with NVCZ. [d] Absorptions due to different isomers are too close to be distinguishable. [e] Data for one isomer which has one ester group in the cis position to the carbazole moiety. [f] Not reliably measured.

These values were plotted against the reduction potentials as measured by cyclic voltammetry (Table II). A linear relationship was observed (Figure 1), proving that these properties are almost independent of steric effects as expected. The sequence

$$\mathbf{1 > 2 \gg 3 \cong 4Z \cong 4E > 5 \gg 6}$$

can be understood by noting that CN is more electron attracting than $COOCH_3$.

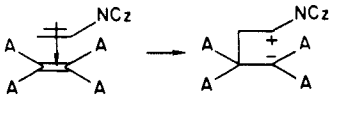
The equilibrium constant for EDA complex formation was measured for the NVCZ-**3** system in dichloromethane at 25 °C by using UV at 438 nm; application of the Benesi–Hildebrand method led to a value of 0.20 L/mol.

Reactions under Organic Chemists' Conditions. Cyclobutane Formation. The electrophilic olefins reacted with equivalent amounts of NVCZ to form cyclobutanes (Table III). When the solution was mixed, variously colored EDA complexes were observed. The reaction solutions ultimately become colorless and occasionally give colorless crystals. Disappearance of the EDA color is a good indication of reaction time. The reactions are faster in more polar solvents, acetonitrile > dichloromethane > benzene, but the reaction in less polar solvents is cleaner. The initial concentrations of NVCZ and the electron-poor olefin and the reaction temperatures were varied somewhat because of varying solubilities and reactivities of the electron-poor olefins.

The relative reactivity order of electron-poor olefins in benzene is shown in Table III. This is the same order as observed for the relative electrophilic character of these olefins.

Identification of the cyclobutanes was accomplished by ^1H NMR spectroscopy (Table IV), ^{13}C NMR spectroscopy (Table V), mass spectrometry, and infrared spectroscopy. The detailed structural assignment of the isomers **2**-Cb-a–d was performed using NMR data as well as data obtained from the isomerization to the corresponding *trans*-1-butenes (see Experimental Section).

The EDA complex readily collapses by bond formation between the β-olefinic carbons to form the gauche tetramethylene:



A = CN, $COOCH_3$

The bond formation will occur so as to form the gauche tetramethylene with the most stabilized terminals: $-C(CN)_2 > -C(CN)COOCH_3 \gg -C(COOCH_3)_2$. Minor inductive stabilization by the adjacent group as well as greater steric interference ($COOCH_3$ > CN) accounts for the detailed sequence.

The cycloaddition of olefin **3** was regiospecific, leading to a single cyclobutane **3**-Cb. Here the adverse steric effect of the two carbomethoxy groups to bond formation is overcome by the resulting electronic stabilization by the $-C(CN)_2$ terminus. Similar regioselection was found by Hall and Sentman in the addition of *p*-methoxystyrene to olefin **3**.[9]

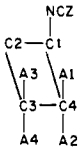
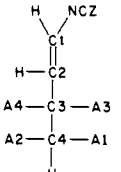
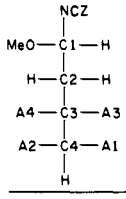
The tetramethylene formation for olefin **2** is not regiospecific, as witnessed by the formation of four isomeric cyclobutanes. Bond

(7) It has been reported in the literature that in some cases both the transition from the highest (λ_1) and second highest molecular orbitals of the donor to the LUMO of the acceptor occur (λ_2). Pearson, J. M.; Turner, S. R.; Ledwith, A. In *Molecular Association*; Forster, R., Ed.; Wiley: New York, 1979; Vol. 2, Chapter 2. The CT absorption maxima in this work correspond to λ_2. The linear relationship observed between the CT absorption maxima and reduction potentials is still valid as we consistently plot λ_2 against E_p for the different donor–acceptor pairs.

(8) Mulvaney, J. E.; Cramer, R. J.; Hall, H. K., Jr., *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 309.

(9) Hall, H. K., Jr.; Sentman, R. C. *J. Org. Chem.* **1982**, *47*, 4572.

Table V. ^{13}C NMR Data of Cyclobutanes, 1-Butenes, and 1-Methoxybutanes[a,b]

compd	isomer	substitutent A1	A2	A3	A4	chemical shift (multiplicity) C1	C2	C3	C4	CN	C=O	OCH_3
	**3-Cb**	CN	CN	E	E	55.20 (d)	32.68 (t)	54.29 (s)	42.00 (s)	112.06, 161.51	165.61, 161.51	
	6-Cb	E	E	E	E	51.33 (d)	31.34 (t)	53.90 (s)	67.09 (s)		169.74, 168.44 168.21, 167.30	
	**1-Bu**	CN	CN	CN	CN	133.77 (d)	96.63 (d)	41.28 (s)	35.69 (d)	107.65, 110.11, 110.93[d]		
	2-Bu-a	CN	CN	CN, E	CN, E	131.85 (d)	101.05 (d)	52.43 (s)	32.03 (d)	112.45, 110.01, 109.27	163.76	
	2-Bu-b	CN, E	CN, E	CN	CN	131.56 (d)	99.62 (d)	38.46 (s)	46.03 (d)	111.31, 111.02, 109.07	160.71	
	3-Bu	CN	CN	E	E	130.32 (d)	106.86 (d)	60.59 (s)	31.12 (d)	110.66[d]	166.07	
	4-Bu-a[c]	CN, E	CN, E	CN, E	CN, E	130.62 (d)	104.20 (d)	50.94 (s)	45.09 (d)	114.01, 112.16	165.84, 162.82	
	4-Bu-b					130.29 (d)	104.22 (d)	50.03 (s)	44.70 (d)	114.01, 112.35	165.06, 162.49	
	**2-MeO-a**	CN	CN	CN, E	CN, E	83.60 (d)	38.66 (t)	42.95 (s)	35.15 (d)	112.5~108.5	~160.6	~56.1 (q)
	2-MeO-b	CN, E	CN, E	CN	CN	83.56 (d)	38.20 (t)	34.76 (s)	43.73 (d)	111.83, 111.54, 110.83	161.26	56.20 (q)
	3-MeO	CN	CN	E	E	83.69 (d)	36.51 (t)	57.60 (s)	27.87 (d)	112.26, 110.99	166.52, 166.20	56.68 (q)
	4-MeO	CN, E	CN, E	CN, E	CN, E	83.66 (d)	40.25 (t)	47.01 (s)	43.82 (d)	115.12, 112.03	166.36, 162.72	

[a] E = $COOCH_3$. Solvent was $CDCl_3$ and data in δ. [b] Data for aromatic carbons are not shown. [c] Diastereomers. [d] Two peaks observed.

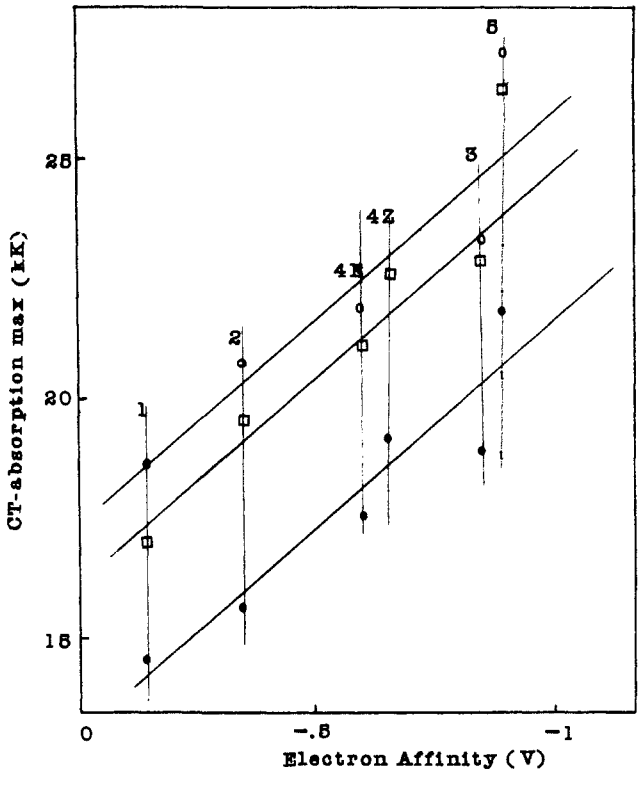
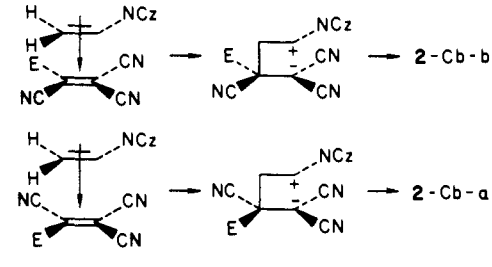


Figure 1. CT absorption maximum (10^{-3} cm^{-1}) of the EDA complexes of tetrasubstituted olefins with donors vs. their reduction potentials: (●) complexes with *N,N*-dimethylaniline, (□) complexes with *N*-ethylcarbazole, (○) complexes with hexamethylbenzene.

formation occurs at both the dicyano, and the cyano, carbomethoxy termini of the olefin, indicating that the electronic stabilization of the carbanion center by (CN, $COOCH_3$) is comparable to that by (CN, CN). From the isomer ratio, we conclude that the latter is preferred by a 60/40 ratio.

In our interpretation we postulate that in the gauche tetramethylene, rotation that the C1–C2 bond does not occur. Huisgen already has shown this to be the case for the propenyl ethers.[1,2] A 20% loss of stereochemistry in the propenyl ethers in the reaction with **1** was observed in polar solvents, while very little loss was seen in nonpolar solvents. Similar results were found for the reaction of anethole with **1** by Bartlett.[3] Huisgen pointed out that C1–C2 rotation would destroy the through-bond coupling which stabilizes the tetramethylene. It seems reasonable that the much bulkier, more electron-donating N-carbazolyl group should also resist C1–C2 bond rotation.

Of the four cyclobutane isomers, **2**-Cb-a and -b only differ in the C1–C3 stereochemistry. If the above postulate is accepted, these two isomers must arise from two diastereomeric tetramethylenes. Their formation from the EDA complexes can be readily understood by sliding the olefin over the face of NVCZ and bonding in either sense:



E = $COOCH_3$, NCz = N-carbazolyl

The C1–C3 cis–trans ester–carbazolyl ratio of 22:39 at room temperature reflects a small steric effect in bond formation.

Similarly, in the four cyclobutane isomers obtained from the cycloaddition of **4Z** and **4E** with NVCZ, the cis–trans ratio for the carbazolyl group at C1 and the ester group at C3 is 41/59 starting from **4Z** and 54/46 from **4E**, again indicating the minor importance of the steric effects in the bond formation.

C3–C4 rotation enables the formation of further isomers. In the **4**-Cb-a–d series, the cis–trans ratio for the carbazolyl group at C1 and the ester group on the adjacent C4 is 32/68 for **4Z** at room temperature and 20/80 for **4E** at 80 °C. This means that C3–C4 rotations are fast enough compared with ring closure to give the sterically less hindered cyclobutanes as major products, even though such rotation would impede the through-bond coupling. Possibly the fact that the acceptor terminal has two substituents permitting almost continuous through-bonding may be responsible for this situation.

One earlier study also saw rotation around the C3–C4 bond in the case of 1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes.[10] On

(10) Proskow, S.; Simmons, H. E.; Cairns, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 5254.

Table VI. *trans*-1-Butene Formation

cyclobutane[a]	conditions: solv	temp, °C	time, h	yield,[b] %	no. of *trans*-1-butene isomers
1-Cb	$CHCl_3$	26	1	100	1
2-Cb-a-d	$CHCl_3$	26	16	100	2
3-Cb	CH_3CN	26	24	100	1
4-Cb-a-d	C_6H_6	80	48	~80	2
	CH_3CN	50	96	~80	
5-Cb (mixture)	DMF	150	8	~50	1
6-Cb	DMF	150	24	0	

[a] Concentrations varied in the range 0.20~0.10 M. [b] Yields are based on ^1H NMR spectra after evaporation of solvent.

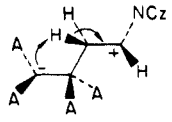


Figure 2. 90°–90° conformation of trans T.

the other hand, Hall and Abdelkader found retention in the reaction of dimethyl cyanofumarate with *p*-methoxystyrene,[11] while Hoffmann and his co-workers obtained preservation from fumaronitrile and maleonitrile with tetramethyoxyethylene.[12] Nivard et al. also studied this problem.[13]

***trans*-1-Butene Formation.** Under more vigorous reaction conditions, the cyclobutanes isomerized to the corresponding *trans*-1-butenes (Table VI). These isomerizations required longer reaction time, more polar solvent, and/or higher temperatures. Cyclobutanes from the more reactive electron-poor olefins isomerized more easily:

1-Cb > **2**-Cb > **3**-Cb > **4**-Cb > **5**-Cb ≫ **6**-Cb (no reaction)

No deuterium was incorporated at C4 when these isomerizations were run in deuterated solvents. This proves intramolecular hydrogen migration from C2 to C4 during *trans*-1-butene formation.

No colors were observed upon dissolution of cyclobutanes or during these reactions except in the case of **1**-Cb (see below).

trans-1-Butenes were also obtained as the secondary products by reacting the parent olefins under similar conditions to those for isomerization products. For example, reaction of **1** with NVCZ in chloroform at 28 °C first produced colorless crystals of **1**-Cb. The system was again homogeneous after another 40 min; at this stage the solution contained only **1**-Bu.

^1H NMR data for the *trans*-1-butenes are summarized in Table VII. The large coupling constants indicate that the 1-butenes are the trans isomers. The data of the ^{13}C NMR, infrared and mass spectra confirm the structure. The fact that all 1-butenes formed are the trans isomers and that proton migration occurs intramolecularly from C2 to C4 strongly suggests that the trans tetramethylene, formed through C2–C3 rotation from the initially formed gauche T (T is the tetramethylene intermediate), is the key intermediate here. For zwitterions the barrier to C2–C3 rotation is given as 3–6 kcal/mol[2]. In the trans T, one of the p orbitals on the C4 anionic terminus faces the hydrogens on C2. Thus, proton transfer to the carbanionic center is facilitated by the trans–antiperiplanar relationship (Figure 2). These results are the first substantial evidence for the occurence of the trans T. Earlier results by Hall and Ykman[14] and by Hall and Abdelkader,[11] as well as the multifarious results of enamine alkylation,[15] all point to the occurrence of trans-T intermediates.

The results show that the cyclobutanes with two cyano groups at C4 (**1**-Cb, **2**-Cb, and **3**-Cb) all isomerize at room temperature; additional cyano substituents at C3 increase the rate. The cyclobutanes (**4**-Cb and **5**-Cb) with one cyano and one carbomethoxy group at C4 react markedly slower. The cyclobutane **6**-Cb with two carbomethoxy groups at C4 does not isomerize to the *trans*-1-butene. Thus, the main factor determining the rate of isomerization is the anion-stabilizing ability of the substituents at C4 (CN > $COOCH_3$). The more stabilized gauche-T forms faster. Less Coulombic attraction exists between the positive charge on C1 and the negative charge on C4 if there are two CN substituents at C4 (more delocalized charge). Therefore, this reduction in Coulombic attraction facilitates C2–C3 rotation to form trans T. Solvation by polar solvent can accomplish stabilization also. Correspondingly the observed trend of cyclobutane reactivity follows that of the parent electron-poor olefins.

Trapping Zwitterionic Tetramethylene with Methanol. When NVCZ is mixed with the electrophilic olefin in methanol, EDA color is observed. The color disappears faster in methanol than in methylene chloride or benzene. The reaction conditions for each olefin pair are summarized in Table VIII. For example, reaction of olefin **2** with NVCZ in methanol is complete after 20 min, compared to 1 h in benzene. The same olefin reactivity order as in benzene was observed:

1 > **2** > **3** > **4E** > **5** ≫ **6**

The primary products are 1-methoxybutanes instead of cyclobutanes, as proven with ^1H NMR by following the reaction.

The yields of 1-methoxybutanes varied depending on the electron-poor olefin used. Complete trapping of the intermediates by methanol was accomplished in the reactions of **1**, **2**, **3**, and **4E** with NVZ, while poorer yields were obtained in the reaction of **5** or **6** due to competitive formation of cyclobutanes.

1-Methoxybutanes obtained from the olefins in deuterated methanol (CH_3OD) are deuterated at C4; as no signal is observed for H4 in NMR, all other signals are unchanged. The same 1-methoxybutanes were formed from the cyclobutanes, but no colors were observed (Table IX). These ring-opening reactions with methanol required more vigorous conditions than 1-methoxybutane formation from the parent olefins. The same reactivity order was found for the cyclobutanes as for the parent olefins:

1-Cb > **2**-Cb > **3**-Cb > **4**-Cb > **5**-Cb ≫ **6**-Cb

All spectral data confirm the structure of the 1-methoxybutanes: ^1H NMR (Table X), ^{13}C NMR (Table V), infrared, and mass spectra.

Formation of 1-methoxybutanes as the primary products from olefins clearly indicates that the addition between NVCZ and electron-poor olefins occurs in a stepwise fashion and that the tetramethylene intermediate T is predominantly zwitterionic. It is still ambiguous in which conformation T is trapped, gauche or trans; in other words, which occurs faster, C2–C3 rotation or addition of methanol. In cases where competitive cyclobutane formation was observed (reactions of **5** and **6**), gauche T has probably been trapped.

For the methanolysis of cyclobutanes the same reactivity order as for the olefins is observed. The anion-stabilizing ability of the substituents at C4 is the main factor; more stabilized gauche T's form faster. Solvation by the polar solvent methanol also accomplishes stabilization.

Polymer Chemists' Conditions. Armed with the preceding knowledge, we selected two olefins to be used in polymerization reactions: TCNE (**1**) and dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (**3**). Both olefins are very reactive and easily available.

Tetracyanoethylene 1 in Excess NVCZ. Upon mixing a solution of **1** with excess NVCZ an intense blue violet solution forms instantaneously. The color faded rapidly (30 s) but did not disappear completely. The reaction product at this point was exclusively the cyclobutane adduct, 1-(carbazol-9-yl)-2,2,3,3-tetracyanocyclobutane (**1**-Cb) as established by isolation. The concentration of the remaining **1** can be calculated from the ratio of EDA absorbance at time zero and after 40 s. The ratio is 560; thus, an equilibrium between the parent olefin and cyclobutane **1**-Cb exists.

The polymerization was followed by size exclusion chromatography (SEC), to obtain the time–conversion curves shown in Figure 3.

(11) Hall, H. K., Jr.; Abdelkader, M. *J. Org. Chem.* **1981**, *46*, 2948.
(12) Hoffmann, R. W.; Bressel, U.; Gehlhaus, J.; Hauser, H. *Chem. Ber.* **1971**, *104*, 873.
(13) Ooms, P. H. J.; Scheeren, J. W.; Nivard, R. J. F. *Synthesis* **1975**, 260, 263.
(14) Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.
(15) Cook, A. G. In *Enamines*; Marcel Dekker: New York, 1969; p 211.

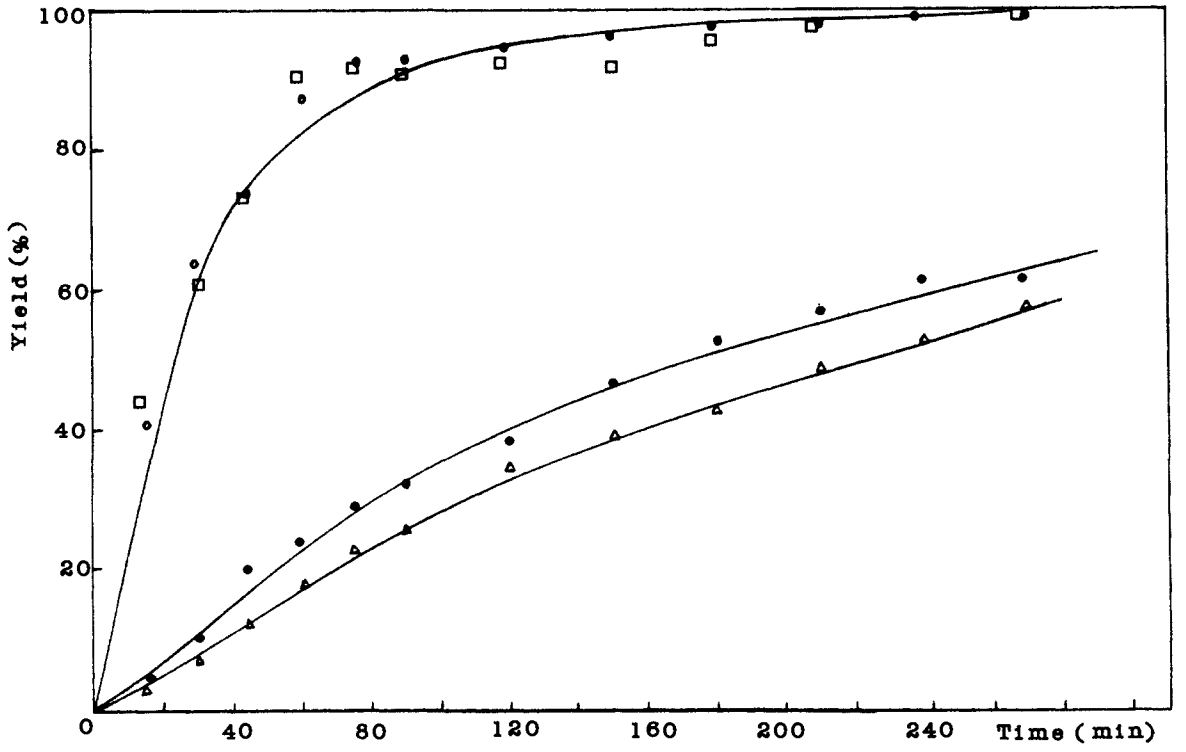


Figure 3. Time–conversion curves of the polymerization of *N*-vinylcarbazole initiated by **1** or **1**-Cb at 30.5 °C in dichloromethane. [**1**] = 0.01 M, [NVCZ] = 0.22 M, (○) polymer, (●) yield of cyclohexane **7**. [**1**-Cb] = 0.01 M, [NVCZ] = 0.21 M, (□) polymer, (△) yield of cyclohexane **7**.

Table VII. ^{1}H NMR Data of *trans*-1-Butenes[a]

isomer	substituent A1	A2	A3	A4	chemical shift δ H1	H2	H4	CH_3 (ester)	coupling const $J_{1,2}$, Hz	solvent
1-Bu	CN	CN	CN	CN	8.07	6.03	4.62		14.0	$CDCl_3/CD_2Cl_2$ (3:1 v/v)
2-Bu-a	CN	CN	CN, E	CN, E	7.56	5.98	4.18	3.91	14.0	$CDCl_3$
2-Bu-b	CN, E	CN, E	CN	CN	7.63	5.88	4.51	3.73	14.0	$CDCl_3$
3-Bu	CN	CN	E	E	7.48	6.39	5.06	3.98[d]	15.0	CD_3CN
4-Bu-a[b]	CN, E	CN, E	CN, E	CN, E	7.58	5.83	4.48	3.77, 3.88	14.0	$CDCl_3$
4-Bu-b	CN, E	CN, E	CN, E	CN, E	7.49	6.33	4.19	3.74, 3.85	16.0	$CDCl_3$
5-Bu[c]	CN, E	CN, E	E	E	7.48	6.49	4.65	3.82, 3.91[d]	15.0	$CDCl_3$

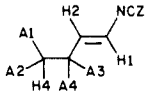
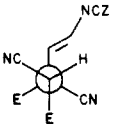
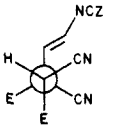
[a]  E = $COOCH_3$. Absorptions of aromatic protons are not shown. The appeared between δ 7.00 and 8.20. [b] Two different absorptions are due to diastereomers  and  [c] Only one structural isomer was obtained. [d] Two peaks observed.

Table VIII. 1-Methoxybutanes from Olefins

olefin	conditions [olefin],[a] M	temp, °C	time, h	EDA color	yield,[b] %	no. of 1-methoxybutane isomers found
1	0.32	26	0.25	purple	100	1
2	0.30	26	0.33	purple	100	2
3	1.00	26	0.50	red	100	1
4E[c]	0.20	26	16	red	~100	1
5	1.00	26	24	orange	~75[d]	1
6	0.20	60	48	yellow	~35[e]	1

[a] 1.1 equiv of NVCZ to electron-poor olefin was used. [b] Yields are based on ^{1}H NMR measurements after evaporation of solvents. [c] Thermal isomerization of **4Z** to **4E** competes with the reaction. [d] With ~25% of **5**-Cb. [e] With ~25% of **6**-Cb.

Table IX. 1-Methoxybutane Formation from Cyclobutanes

cyclobutanes[a]	conditions temp, °C	time, h	yield,[b] %	no. of 1-methoxybutane isomers found
1-Cb	26	0.25	100	1
2-Cb	26	2	100	2
3-Cb	50	18	100	1
4-Cb	60	20	85	1
5-Cb	60	36	~80	1
6-Cb	60	72	<10	1

[a] Concentrations varied in the range of 1.00~0.10 M. The reactions of **1**-Cb were initially heterogeneous, and the system was homogeneous within 5 min. [b] Refer to footnote *b* of Table VI.

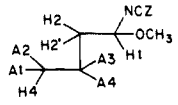
The cyclobutane **1**-Cb was still reactive. Left in solution with excess NVCZ, it disappeared at a moderate rate with concomitant formation of poly(NVCZ) and a 2:1 adduct, 1,3-di(carbazol-9-yl)-5,5,6,6-tetracyanocyclohexane (**7**). This cyclohexane derivative **7** was established as a single isomer (diequatorial) by ^{1}H and ^{13}C NMR spectroscopies (See Experimental Section).

The polymerization proceeds at the same rate when NVCZ is mixed with **1** itself. The cyclohexane derivative **7** is also formed in this case, but again no 1-butene **1**-Bu is observed.

The proposed mechanism is shown in Scheme I. Trans T forms the hexamethylene intermediate by adding a second NVCZ

Table X. ^{1}H NMR Data of 1-Methoxybutanes[a]

	substituent				chemical shift δ						coupling const, Hz			
isomer	A1	A2	A3	A4	H1	H2	H2′	H4	OCH_3	CH_3 (ester)	$J_{1,2}$	$J_{2,2'}$	$J_{1,2'}$	solvent
1-MeO	CN	CN	CN	CN	6.09	3.43	2.55	4.99	3.40		10.0	14.5	3.5	$CDCl_3$
2-MeO-a	CN	CN	CN	E	6.08	3.22	2.68	4.88	3.33	3.92	9.5	15.0	4.0	$CDCl_3/CD_3CN$ (1:1 v/v)
2-MeO-b	CN	E	CN	CN	6.10	3.34	2.66	4.69	3.33	3.92	10.0	15.0	4.0	$CDCl_3/CD_3CN$ (1:1 v/v)
3-MeO	CN	CN	E	E	6.07	3.28	2.62	4.90	3.25	3.82, 3.95	9.5	15.0	3.0	$CDCl_3$
4-MeO[b]	CN, E	CN, E	CN, E	CN, E	5.93	3.25	2.39	4.35	3.22	3.86, 3.97	10.0	14.0	2.5	$CDCl_3$
5-MeO[c]	CN, E	CN, E	E	E	6.17	3.17	2.62	4.68	3.10	3.75, 3.86, 3.99	10.0	14.5	2.5	$CDCl_3$
6-MeO	E	E	E	E	5.77	obscured	obscured	4.25	3.52	3.80 (d) 3.90 (d)				$CDCl_3$

[a] 

E = $COOCH_3$. Aromatic hydrogen absorptions appeared in the range δ 7.00–8.20. [b] Diastereomers showed identical absorptions. [c] One of two possible structural isomers was obtained. [d] Two peaks observed.

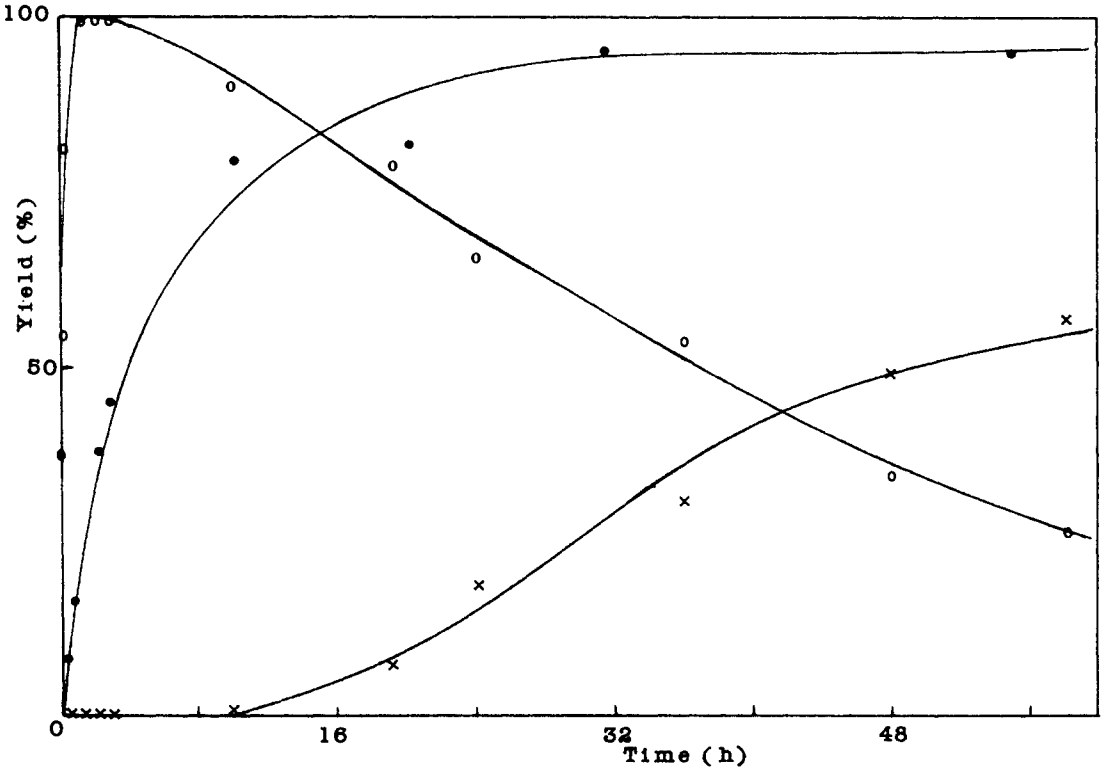


Figure 4. Time-conversion curves for the TCNE–NVCZ-3 reaction in dichloromethane at 30.5 °C [3] = 0.10 M, [NCVZ] = 0.40 M, (●) polymer yield calculated for 0.3 M NVCZ, (o) yield of cyclobutane 3-Cb, (×) yield of *trans*-1-butene derivative 3-Bu calculated for 0.10 M 3.

molecule. The hexamethylene is the intermediate for both the cyclohexane adduct formation and the initiation of the cationic polymerization of NVCZ.

Our conclusions regarding the 1–NVCZ system could not be made completely quantitative for several reasons: (1) the cycloaddition is too fast, (2) the tetramethylene intermediate T can revert back to the EDA complex and the starting olefins, and (3) the cyclobutane is unstable on silica gel. Thus, HPLC cannot be used to follow the disappearance of the small molecules. Accordingly, we turned to the less reactive electrophilic olefin 3.

Dimethyl 2,2-Dicyanoethylene-1,1-dicarboxylate (3) in Excess NVCZ. An intense red color (λ_{max} 430~458 nm, depending on the solvent) is formed upon mixing solutions of the reactants. The intensity of the EDA absorption λ_{max}, followed by UV spectrometry, decayed exponentially and eventually reached zero after 45 min. The resulting colorless solution contained cycloadduct 3-Cb quantitatively. This cyclobutane, 3-Cb, left in solution with excess NVCZ, decayed with formation of homopoly(NVCZ) and isomeric 1-butene, *trans*-dimethyl 1-(carbazol-9-yl)-4,4-dicyano-1-butene-3,3-dicarboxylate (3-Bu). 3-Cb was less reactive than 1-Cb. The reaction mixture was analyzed by SEC and by HPLC (silica column). The polymer could be analyzed with SEC; 3-Cb and 3-Bu overlapped with NVCZ. However, in HPLC chromatograms, 3-Cb and 3-Bu were satisfactorily separated from the remaining NVCZ and the standard *p*-nitroaniline. Thus, all the components could be followed, and this reaction system was eminently suitable for kinetic and mechanistic studies (Figure 4).

No color was observed when 3-Cb was dissolved in a NVCZ solution. 3-Cb could initiate the polymerization at the same rate as 3. The rate of isomerization of 3-Cb to *trans*-1-butene 3-Bu in deuterated dichloromethane in the absence of NVCZ was measured by ^{1}H NMR spectroscopy. The rate was first order in 3-Cb, and the rate constant is $\sim 5 \times 10^{-6}$ s^{-1} at 30 °C. The rate of consumption of 3-Cb in dichloromethane in the presence of a large amount of NVCZ, thus under polymerizing conditions, was measured by HPLC using *p*-nitroaniline as standard. A first-order rate constant was found, $\sim 5 \times 10^{-6}$ s^{-1}, identical with the value above.

Initial polymerization rates $R_p°$ were measured by SEC with varying concentrations of 3-Cb. $R_p°$ were calculated from the

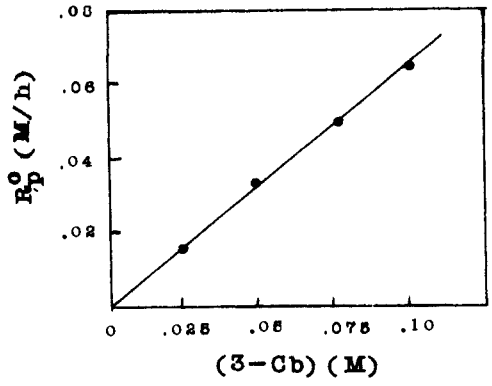


Figure 5. Initial polymerization rates of NVCZ initiated by varying concentrations of cyclobutane 3-Cb in dichloromethane at 30.5 °C, [NVCZ] = 0.30 M.

initial slopes of plots of polymer yields vs. time at various initial concentrations of 3-Cb. Figure 5 clearly demonstrates the first-order dependence of the initial rate on 3-Cb concentration. The initial polymerization rates were also measured with varying NVCZ concentrations. Figure 6 shows that the order of dependence of $R_p°$ on $[NVCZ]_0$ ranges from 2.0 at higher concentrations to 2.8 at lower NVCZ concentrations. $R_p°$ can thus be expressed by

$$R_p° = k[3\text{-Cb}]_0^{1}[NVCZ]_0^{2.0-2.8} \quad (1)$$

where k is an overall rate constant and $[3\text{-Cb}]_0$ and $[NVCZ]_0$ are the initial concentrations.

Considering that the formation of 3-Bu and the hexamethylene intermediate (initiation) are competing, we derive the following expression for the rate of initiation

$$R_i = k_i(k_c[3\text{-Cb}]_t)\frac{k_i[NVCZ]_t}{k_b + k_i[NVCZ]_t}[NVCZ]_t \quad (2)$$

where k_c, k_i, and k_b are the rate constants for formation of trans T, hexamethylene, and 3-Bu, respectively, and $[NVCZ]_t$ and $[3\text{-Cb}]_t$ are the concentrations of NVCZ and cyclobutane 3-Cb at time t, respectively. The first term $k_c[3\text{-Cb}]_t$ expresses the rate of trans T formation, and the second term $k_i[NVCZ]_t/(k_b + k_i[NVCZ]_t)$ is derived on the partitioning of the trans T between isomerization to the 1-butene and addition of monomer.

First-order dependence of $R_p°$ on $[3\text{-Cb}]_0$, as shown, indicates ion-pair propagation and recombination termination. The termination rate R_t can be expressed as

$$R_t = k_t[P_n^+X^-] \quad (3)$$

where k_t and $[P_n^+X^-]$ are the rate constants for termination and the concentration of ion-pair propagating species, respectively. We make a steady-state approximation here

$$R_i = R_t$$

Thus,

$$[P_n^+X^-] = \frac{k_c k_i^2}{k_t}[3\text{-Cb}]_t\frac{[NVCZ]_t^2}{k_b + k_i[NVCZ]_t} \quad (4)$$

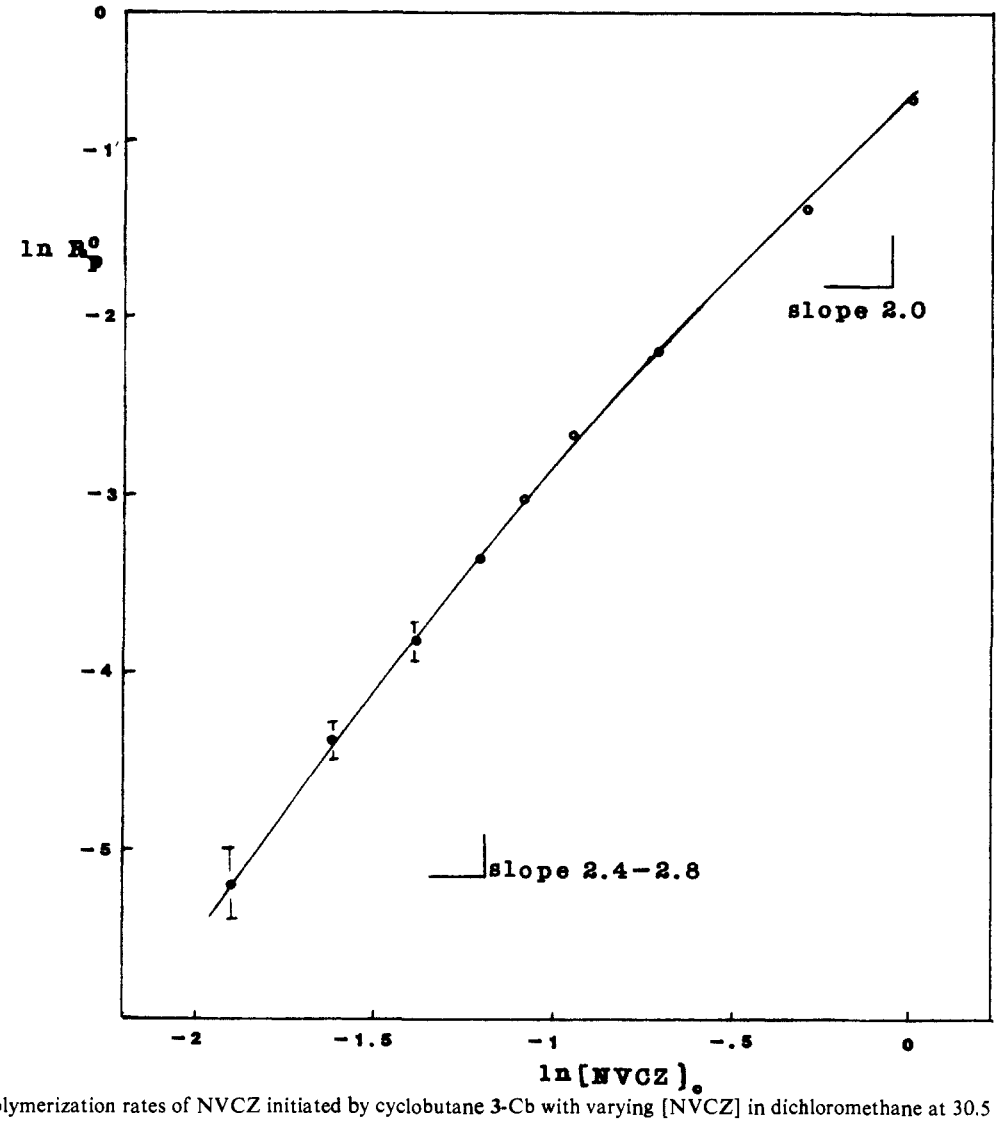


Figure 6. Initial polymerization rates of NVCZ initiated by cyclobutane 3-Cb with varying [NVCZ] in dichloromethane at 30.5 °C, $[3\text{-Cb}]_0$ = 0.05 M.

and

$$R_p = k_p[P_n^+X^-][NVCZ]_t = \frac{k_c k_i^2 k_p}{k_t}[3\text{-Cb}]\frac{[NVCZ]_t^3}{k_b + k_i[NVCZ]_t}$$

We obtain

$$R_p^\circ = \frac{k_c k_i^2 k_p}{k_t}[3\text{-Cb}]_0\frac{[NVCZ]_0^3}{k_b + k_i[NVCZ]_0}$$

This last equation indicates that the dependence of R_p^0 on $[NVCZ]_0$ is not always constant. If $[NVCZ]_0$ is high enough so that $k_b \ll k_i[NVCZ]_0$, then initiation is dominant over the formation of 3-Bu and

$$R_p^0 = \frac{k_c k_i^2 k_p}{k_t}[3\text{-Cb}]_0[NVCZ]_0^2$$

If $[NVCZ]_0$ is low enough so that $k_b \gg k_i[NVCZ]_0$, then the formation of 3-Bu is dominant over initiation,

$$R_p^0 = \frac{k_c k_i^2 k_p}{k_b k_t}[3\text{-Cb}]_0[NVCZ]_0^3$$

Our proposed mechanism explains the results both qualitatively and quantitatively. The kinetic equation makes two predictions. First, the polymerization rate should be first order in the cyclobutane initiator. Figure 5 shows this to be the case. The line passes through the origin, as it must. Second, the rate should be second order in NVCZ concentration at high concentrations and third order at low concentrations. Figure 6 shows that the rate is second order at high concentrations and tends toward third order at the lowest concentration which were experimentally feasible.

Compared with the reaction of NVCZ with **1**, the reaction of NVCZ with **3** proceeds more slowly and went completely to cyclobutane as the kinetically favored product. Its subsequent reaction with excess NVCZ led to the competitive formation of homopoly(NVCZ) and 1-butene. The small molecule 3-Bu forms by the way of the trans tetramethylene. The antiperiplanar stereoelectronic effect in the transition state makes this very reasonable. The competing reaction of the trans tetramethylene is addition of a second NVCZ molecule to form the hexamethylene intermediate, which in this case does not cyclize. The hexamethylene initiates the cationic polymerization of NVCZ.

Summary and Conclusions

The thermal, spontaneous reactions of *N*-vinylcarbazole (NVCZ) with the seven electrophilic tetrasubstituted olefins containing cyano and/or carbomethoxy groups were investigated. The relative electrophilicities of the olefins were established as **1** > **2** ≫ **3** ≅ **4Z** ≅ **4E** > **5** ≫ **6**, through measurements of their electron donor–acceptor complexing abilities and their reduction potentials. This same order was found for their reaction rates with *N*-vinylcarbazole.

Small Molecule Formation. When equimolar amounts (organic chemists' conditions) were employed, the reactions proceeded in the following sequence: instantaneous formation of the electron donor–acceptor complex, formation of the cyclobutane adduct, and isomerization to a *trans*-1-butene derivative. The reaction of NVCZ with these seven olefins in methanol trapped the tetramethylene intermediate to yield 1-methoxybutane derivatives. The cyclobutane adducts in methanol gave these same methoxybutanes.

The proposed mechanism involves formation of the overlapped donor–acceptor complex and its collapse by bond formation at the terminals to form a zwitterionic tetramethylene in gauche conformation, which closes reversibly to cyclobutane. Harsher reaction conditions lead to isomerization of gauche T to trans T and the formation of *trans*-1-butene.

Polymerization. Left in excess, *N*-vinylcarbazole solution (polymer chemists' conditions), the olefins, or the corresponding cyclobutane cycloadducts initiated homopolymerization of NVCZ. The reaction of excess NVCZ with tetracyanoethylene **1** in dichloromethane solution led to homopolymer and a 2:1 adduct. Cyclobutane **1**-Cb, placed in solution with excess NVCZ, gave identical results.

Dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (**3**) reacted more slowly with excess NVCZ. This reaction was quantitative, as evidenced by the complete disappearance of EDA complex color and led exclusively to cyclobutane **3**-Cb. This cyclobutane, left in solution with excess NVCZ, disappeared very slowly with competitive formation of the *trans*-1-butene derivative and homopoly(NVCZ). The rate law for this reaction was

$$R_p^0 = k[3\text{-Cb}]_0^1[NVCZ]_0^{2-3}$$

This equation was derived on partitioning the trans tetramethylene between isomerization to the 1-butene and successive addition of monomer.

Our results demonstrate conclusively that neither the EDA complex nor the ion–radical pair possibly formed by single electron transfer (SET) (literature reviews in ref 16, 17,18) have anything to do with initiation. Polymerization is occurring at its maximum rate long after the EDA complex concentration has diminished to an extremely small value. Further, the cyclobutane's ability to initiate at equal rates under conditions where no EDA at all is present shows that the EDA or ion radical pair are irrelevant to initiation.[6,19]

Selected Mechanism. Two other mechanisms for these charge-transfer initiations can be found in the literature.

The first mechanism of electron transfer to form ion radicals which then initiate the observed polymerizations has been proposed. *N*-Vinylcarbazole and the electrophilic tetrasubstituted ethylenes of this study should represent the most favorable situation for such SET chemistry, inasmuch as the ion radicals from these components are well-known. However, no evidence for the involvement of ion radicals in this work was found.

A second mechanism involving propagation via the excited electron donor–acceptor complex[20] has received no support in either the literature or the present work.

On the contrary, our data show impressive support for our mechanism of bond-forming initiation. Combined with its ability to correlate a vast body of organic and polymer chemistry literature,[4] it presents a satisfactory solution to the problem of charge-transfer initiation.

Experimental Section

Instrumentation. All melting points were determined in open capillary with a Melt-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer (Model 710A or 983). ^{1}H NMR spectra were obtained either on a Varian T-60 Analytical NMR spectrometer or a Bruker Model WM-250 multinuclear FT spectrometer. The former instrument was mostly used to follow the reaction in preliminary experiments, and the spectral and kinetic data were obtained with the latter instrument. ^{13}C NMR spectra have been recorded on a Bruker WH-90 QPDFT spectrometer at 22.63 MHz. Mass spectra were determined on a Varian No. 311A Mass Spectrometer. HPLC analysis was done on an IBM Silica Standard column (4.5 × 250 mm); SEC analysis was performed on Du Pont ZORBAX PSM 60-S and/or PSM100-S columns (250 mm). Detectors were Waters Assoc. Differential Refractometer or Spectra Physics 8200 UV (254-nm) detector. The eluent was *n*-hexane/acetone for HPLC and chloroform or benzene for SEC. UV spectroscopic work was done with a Perkin-Elmer Model 552 spectrometer, using quartz cells of 1- or 10-mm thickness with a solution container at constant temperature. Elemental analyses were performed by Micanal, Tucson, AZ, or by Atlantic Microlab, Inc., Atlanta, GA.

Chemicals. All the solvents used in this work were purified by distillation in the presence of appropriate drying reagents under nitrogen atmosphere and stored in capped flasks. Chloroform and dichloro-

(16) Review: Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley Interscience: New York, 1982.
(17) Review: Shirota, Y.; Mikawa, H. *J. Macromol. Sci., Rev. Macromol. Chem.* **1977**, *C16*, 129.
(18) Review: Shirota, Y. *Encycl. Polymn. Sci. Technol.* **1985**, *3*, 327.
(19) Nakamura, T.; Soma, M.; Onishi, T.; Tamaru, K. *Makromol. Chem.* **1979**, *135*, 241.
(20) Gaylord, N. G. *J. Polym. Sci.* **1970**, *C31*, 247.

methane were washed with concentrated sulfuric acid, aqueous solution of sodium hydroxide, and water before distillation. All deuterated solvents were used as received.

NVCZ was obtained from Polysciences and was purified by recrystallizations: NVCZ was dissolved in *n*-hexane at room temperature, filtered by passing through activated carbon layer on a filter paper, and placed in a freezer (−50 °C) in the dark. NVCZ plate crystals were collected and dried under vacuum. The purity of NVCZ was checked with SEC and HPLC (no impurities could be detected). The unpurified material showed the presence of considerable amounts of oligomers. Mp: 63.0–64.0 °C [lit. mp 64.0–65.0 °C].

Tetracyanoethylene **1** was purchased from Aldrich and was purified by two successive sublimations (120–130 °C/0.5 mmHg) through an activated carbon layer. Mp: 198–200 °C [lit. mp 198–200 °C].

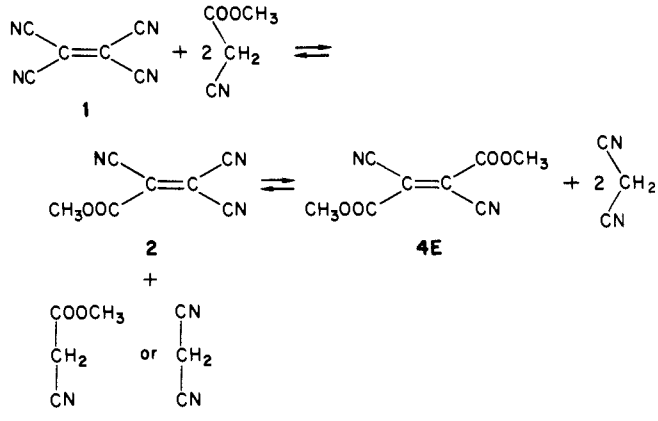
Dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate (**3**) was prepared and purified according to the literature.[9] Bp: 65–70 °C/0.05 mmHg [lit. bp 75–76 °C/0.05 mmHg].

Dimethyl dicyanofumarate **4E** was synthesized by the method reported[21] and was purified by repeated recrystallizations from an acetone/methanol mixture and by sublimations under the same condition as **1**. Mp: 176–178 °C [lit. mp 175–176 °C].

Trimethyl cyanoethylenetricarboxylate **5** was prepared by a modified method.[22] Knoevenagel condensation between dimethyl ketomalonate and methyl cyanoacetate afforded the hydrate, which was dehydrated with an equal weight of P_2O_5 at 160 °C/760 mmHg for 1.5 h, and the olefin was sublimed at 140 °C/0.1 mmHg. Mp: 75–76 °C [lit. mp 77–78 °C].

Tetramethyl ethylenetetracarboxylate **6** was prepared and purified as reported.[23] Mp: 118–118.5 °C [lit. mp 118.5–119.5 °C].

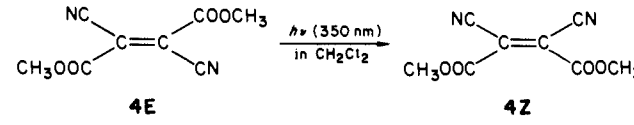
Synthesis of New Electron-Poor Olefins. Methyl tricyanoethylenecarboxylate **2** was synthesized by exchange reactions, analogous to the retro-Michael addition,[24] either from tetracyanoethylene **1** with methyl cyanoacetate (A) or from dimethyl dicyanofumarate **4E** with malononitrile in acetic acid at 100 °C (B). This new olefin is very soluble, even in nonpolar solvents.



A. Tetracyanoethylene **1** (1 g, 7.8 mmol) was dissolved in 10 mL of acetic acid at 100 °C. Methyl cyanoacetate (0.773 g, 7.8 mmol) was added dropwise within 2 min. Stirring was continued for an additional 5 min. The reaction mixture was poured into 300 mL of ice–water. A white solid precipitated and was collected, washed with 100 mL of cold water, and extracted with diethyl ether (100 mL). The ether extract was washed 3 times with 100 mL of cold water (these operations eliminate or wash out insoluble starting material) passed through activated carbon and recrystallized from a diethyl ether/*n*-hexane mixture (1:5 in volume). Yield: 507 mg (40.4%). Mp: 90–93 °C. IR (KBr): 3040, 2950, 2255 and 2215 (CN), 1755 (C=O str.) 1680, 1599 (C=C str.), 1438 (CH_3), 1305, 1242 (ester str.), 1118 and 1010 (ester str.) 890, 780 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.08 (s). ^{13}C NMR ($CDCl_3$): δ_{C_1} 131.46 (s), δ_{C_2} 106.54 (s), δ_{CN} 110.73 (s), 109.50 (s), 108.36 (s), δ_{CH_3} 55.55 (q), $\delta_{C=O}$ 156.39 (s). Anal. Calcd for $C_7H_3N_3O_2$: C, 52.18; H, 1.88; N, 26.08. Found: C, 51.91; H, 1.97; N, 25.89.

B. To a stirred solution of 1 g (5.15 mmol) of **4E** in 10 mL of acetic acid at 100 °C, 3.4 g (51.5 mmol) of malononitrile was added at once. After 30 min, the reaction mixture was worked up in the same manner as above. Unreacted **4E** (400 mg) was recovered, but longer reaction time reduced the yield of **2** by forming water-soluble byproduct. Yield: 249 mg (30.0%). Although the yield was low, this method is more convenient because of the easy preparation of **4E**.

Dimethyl dicyanomaleate **4Z** was synthesized through photoisomerization of dimethyl dicyanofumarate **4E** sensitized with 1,4-dicyanobenzene. A polar solvent such as acetonitrile (D = 38.8) induced thermal isomerization from **4Z** to **4E**, in which **4Z** is thermally stable in dichloromethane or benzene.



4E **4Z**

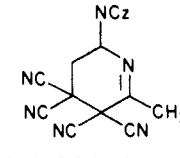
A solution of 1.94 g (10.0 mmol) of **4E** and 1.28 g (10.0 mmol) of 1,4-dicyanobenzene (triplet sensitizer, E_T = 70.5 cal/mol) in 200 mL of dichloromethane was photoirradiated with a Rayonet photochemical reactor at 350 nm, in a Pyrex photoreaction cell (optical path length, 1 cm) at 40 °C. Optical densities of methylene chloride solutions of **4E** and 1,4-dicyanobenzene are 0.45 and 2.60 at 350 nm, respectively. Thus, 1,4-dicyanobenzene was mostly photoexcited. The solvent was evaporated after irradiation for 3 days. The resulting white solid contained the maleate in 95% yield. Diethyl ether (200 mL) was added to the solid mixture and stirred and then 400 mL of *n*-hexane was added. The suspension was slowly evaporated at room temperature to reduce the volume to 400 mL and filtered to remove unreacted **4E**. Pure **4Z** was obtained after two more purifications, filtration, and recrystallization. Yield: 1.63 g (84.0%). Mp: 36.0~38.0 °C. IR (KBr): 2950, 2225 (CN, weak), 1745 (C=O str.), 1440 (CH_3), 1285 (ester str.), 1020 (ester str.) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.94. ^{13}C NMR ($CDCl_3$): $\delta_{C=C}$ 132.79 (s), δ_{CN} 111.09 (s), δ_{CH_3} 54.84 (q), $\delta_{C=O}$ 158.01 (s). Anal. Calcd for $C_8H_6N_2O_4$: C, 49.49; H, 3.12; N, 14.43. Found: C, 49.47; H, 3.02; N, 14.95.

General Reaction Procedure. Calculated amounts of electron-poor olefin and NVCZ were placed separately into a Y-shaped polymerization tube with solvent. The system was evacuated and filled with dry nitrogen. This procedure was repeated. Then the two olefin solutions were combined, and the mixture was stirred continuously. Effects of oxygen and light were examined, and no effect was observed. The reaction in deuterated solvents was followed by ^1H NMR in the case of relatively soluble electron-poor olefin. The disappearance of CT color and complete consumption of electron-poor olefin occurred at the same time. Analytical samples were obtained after evaporation of solvent at room temperature and recrystallization from suitable solvent. Reactions of cyclobutanes and *trans*-1-butenes and the polymerization were run and followed in a similar manner.

Isolation and Identification of the Reaction Products. The specific conditions for each reaction are summarized in the tables. Only the workup is described below.

1-(Carbazol-9-yl)-2,2,3,3-tetracyanocyclobutane (1-Cb). Benzene was continuously evaporated during the reaction up to one-fifth of the original volume. Crystals were then collected and recrystallized from a chloroform/*n*-hexane mixture at −50 °C. All of the above recrystallization operations should be done quickly because **1**-Cb can react further under these conditions. Yield: 82% (white fibroid crystal). Mp: >120 °C dec. (turned to violet upon heating) [lit. mp 120 and 130–131 °C]. IR (KBr): 2220 (weak, CN str.) 1600, 755, 730 cm^{-1}. MS (15 eV): 193 ($NVCZ^{+\bullet}$ main), 167 ($NHCZ^{+\bullet}$). Anal. Calcd for $C_{20}H_{11}N_5$: C, 74.76; H, 3.45; N, 21.79. Found: C, 74.70; H, 3.73; N, 21.09.

Comment: Reaction of **1** or **2** with NVCZ in acetonitrile led to an unidentified product which was not a cyclobutane derivative. Although we could not isolate this compound, the IR spectrum showed the presence of an imine (C=N) at 1680 cm^{-1} as well as cyano and carbazole ring absorptions, and ^1H NMR shows a methyl group at δ 1.94 (singlet). Analogous to the compound found in the vinyl ether system by Huisgen,[1] the following structure is proposed:



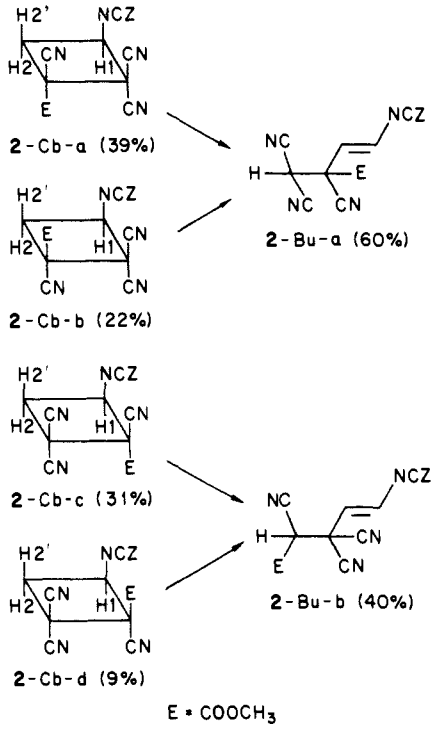
Methyl 1-(Carbazol-9-yl)-2,2,3-tricyanocyclobutane-3-carboxylate (2-Cb-a and -b) and Methyl 1-(Carbazol-9-yl)-2,3,3-tricyanocyclobutane-2-carboxylate (2-Cb-c and -d). After reducing the volume of the solution to one-fifth of the original volume *n*-hexane was added, and the solution was kept in a freezer for 3 days. A cyclobutane mixture of **2**-Cb-a, **2**-Cb-b, **2**-Cb-c, and **2**-Cb-d was obtained as white crystals. Attempted separation by column chromatography failed due to their high reactivity. Yield: 91%. Mp: 95–97 °C. IR (KBr): 2250 (CN), 1760 (C=O), 1260, 755, 730 cm^{-1}. Anal. Calcd for $C_{21}H_{14}N_4O_2$: C, 71.18;

(21) Ireland, C. J.; Jones, K.; Pizey, J. S. *Synth. Commun.* **1976**, *6*, 185.
(22) Sentman, R. C. Ph.D. Thesis, University of Arizona, Tucson, 1982.
(23) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.
(24) Junek, H.; Vray, G.; Zuschnig, G. *Liebigs Ann. Chem.* **1983**, 154.

H, 3.98; N, 15.81. Found: C, 71.56; H, 4.42; N, 15.12.

Structural assignments of isomers **2-Cb-a**, **-b**, **-c**, and **-d** were performed in the following way. Cyclobutane **3-Cb** showed absorptions of two ester methyls on C3 around δ 4.00, and **6-Cb** showed absorptions of three ester methyls around δ 3.85 and one at δ 2.99 which was greatly shifted to higher field. This shifted absorption was attributed to the ester methyl on C4 cis to the carbazolyl group, i.e., the ester and carbazolyl group are cis on vicinal carbons. The cyclobutane isomer showing this shift was assigned to structure **2-Cb-d**. A **2-Cb** mixture of known composition by ^{1}H NMR spectroscopy (39% of a , 22% of b, 31% of c, and 9% of d) was allowed to isomerize to the *trans*-1-butene mixture **2-Bu**. The product consisted of 60% **2-Bu-a** and 40% **2-Bu-b**. During this isomerization, reversions from **2-Cb** to parent olefins do not occur. Thus, in the ester and carbazolyl groups, **2-Cb-c** are also on vicinal carbons but are trans.

Structural assignments of the other cyclobutanes (ester and carbazolyl groups on opposite carbons) are based on the chemical shifts of the ester methyl and H2′ in the ^{1}H NMR spectra. One of these cyclobutanes shows both the ester methyl and the H2′ absorptions at lower field than the other one. These shifts are due to the deshielding effect of the carbazolyl group on the ester methyl and of the carbonyl group on H2′. This cyclobutane has been assigned as **2-Cb-b** and the other one as **2-Cb-a**.



Dimethyl 1-(Carbazol-9-yl)-2,2-dicyanocyclobutane-3,3-dicarboxylate (3-Cb). After the reaction, benzene was evaporated to give oily material, which was recrystallized from dichloromethane/diethyl ether/*n*-hexane. Yield: 65% (white crystals). Mp: 139–142 °C. IR (KBr): 2965, 1767, 1745, 1300, 755, 730 cm^{-1}. MS (70 eV): 387 (M^+) 322 (M^+ - •CH(CN)$_2$), 262 (322 - CH_3COOH), 243, 193 ($NVCZ^{+\bullet}$, main). Anal. Calcd for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.42; N, 10.85. Found: C, 68.42; H, 4.46; N, 10.78.

Dimethyl 1-(Carbazol-9-yl)-2,3-dicyanocyclobutane-2,3-dicarboxylate (4-Cb-a, -b, -c, and -d). After evaporation of benzene, crude crystals were dissolved in dichloromethane/diethyl ether/*n*-hexane and were obtained at −10 °C. Yield: from **4Z** 84%, from **4E** 80%. Mp: 118–119 °C (from **4Z**), 127–129 °C (from **4E**) (turned red). IR (KBr): 2950, 1760, 1740, 1263, 755, 730 cm^{-1}. MS (70 eV): 387 (M^+, main), 360 (M^+ - HCN), 328 (M^+ - •COOCH$_3$), 289 (M^+ - •CH(CN)(COOCH$_3$)), 229 (289 - CH_3COOH), 193 ($NVCZ^{+\bullet}$), 167 ($NHCZ^{+\bullet}$). Anal. Calcd for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.42; N, 10.85. Found: C, 68.36; H, 4.48; N, 10.79.

Olefins **4Z** and **4E** formed four stereoisomeric cyclobutanes. The cyclobutanes **4-Cb-c** and **-d** showed ester methyl proton signals at higher field, indicating that these ester groups at C4 are cis to carbazolyl groups on adjacent carbon C1. The geometry at C3 was determined in the way described above for **2-Cb-a** and **-b**, namely by examining the chemical shifts of ester methyls on C3 and of the H2′ atoms.

Trimethyl 1-(Carbazol-9-yl)-2-cyanocyclobutane-2,3,3-tricarboxylates and Trimethyl 1-(Carbazol-9-yl)-3-cyanocyclobutane-2,2,3-tricarboxylate (5-Cb). After the reaction, benzene was evaporated to give crude white crystals, which were recrystallized from diethyl ester/*n*-hexane. Yield: 76%. Mp: 158–160 °C. IR (KBr): 2955, 2920, 1755, 1738, 1270, 755, 730 cm^{-1}.

Tetramethyl 1-(Carbazol-9-yl)cyclobutane-2,2,3,3-tetracarboxylate (6-Cb). After the reaction, benzene was evaporated to give white massive crystals, containing unreacted parent olefin. **6** was eliminated from the system as the early formed crystals during recrystallization in acetone/diethyl ether/carbon tetrachloride. Final recrystallization could be done from dichloromethane/pentane. Yield: 31%. Mp: 173–175 °C. IR (KBr): 2950, 1735, 1265, 755, 730 cm^{-1}. MS (15 eV): 453 (M^+), 193 ($NVCZ^{+\bullet}$, main). Anal. Calcd for $C_{24}H_{23}N_1O_8$: C, 63.57; H, 5.11; N, 3.09. Found: C, 63.28; H, 4.88; N, 3.05.

***trans*-1-(Carbazol-9-yl)-3,3,4,4-tetracyano-1-butene (1-Bu).** After the volume of chloroform was reduced, diethyl ether and *n*-hexane were added to the reaction mixture. Keeping the solution in the freezer afforded white crystals. Yield: 88%. Mp: 140–145 °C. IR (KBr): 2900, 2230, 1655 (C=C str.), 1622, 1587, 755, 730 cm^{-1}. MS (5 eV): 321 (M^+), 294 (M^+ - HCN, main), 257, 167 ($NHCZ^+$).

***trans*-Methyl 1-(Carbazol-9-yl)-3,4,4-tricyano-1-butene-3-carboxylate (2-Bu-a) and *trans*-Methyl 1-(Carbazol-9-yl)-3,3,4-tricyano-1-butene-4-carboxylate (2-Bu-b).** After evaporation of chloroform, small amounts of diethyl ether and *n*-hexane were added to the oily residue. White crystals were obtained after a week at −50 °C. Yield: 35%. Mp: 112–115 °C. IR (KBr): 3073 (=C—H str.), 2933, 2236, 2218, 1760, 1665 (C=C str.), 1625, 1260, 966, 755, 730 cm^{-1}.

***trans*-Dimethyl 1-(Carbazol-9-yl)-4,4-dicyano-1-butene-3,3-dicarboxylate (3-Bu).** After the reaction, acetonitrile was evaporated to give viscous oil, which was recrystallized from diethyl ether/carbon tetrachloride/*n*-hexane at room temperature (colorless plate crystals). Yield: 49%. Mp: 155–156 °C. IR (KBr): 3050 (=C—H str.), 2950, 2922, 1760, 1740, 1660 (C=C str.), 1625, 960, 755, 730 cm^{-1}. MS (20)V): 387 (M^+), 322 (M^+ - •CH(CN)$_2$, main), 262 (322 - CH_3COOH), 204, 167 ($NHCZ^{+\bullet}$). Anal. Calcd for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.42; N, 10.85. Found: C, 68.31; H, 4.46; N, 10.80.

***trans*-Dimethyl 1-(Carbazol-9-yl)-3,4-dicyano-1-butene-3,4-dicarboxylate (4-Bu).** After reaction of **4-Cb** in benzene or in acetonitrile, solvents were evaporated. The remaining colorless viscous oil was dissolved in diethyl ether/pentane mixture, and the solution was concentrated. White crystals were obtained by gradual evaporation of solvent at room temperature for a week. Yield: 43%. Mp: 130–133 °C. IR (KBr): 3060 (=C—H str.), 2960, 2925, 2275, 1750, 1660 (C=C str.), 1625, 1250, 950, 755, 730 cm^{-1}. MS (20 eV): 387 (M^+), 360 (M^+ - HCN), 289 (M^+ - •CH(CN)COOCH$_3$, 229 (289 - CH_3COOH), 194, 167 ($NHCZ^{+\bullet}$). Anal. Calcd for $C_{22}H_{17}N_3O_4$: C, 68.21; H, 4.42; N, 10.85. Found: C, 69.06; H, 4.59; N, 9.69.

***trans*-Trimethyl 1-(Carbazol-9-yl)-4-cyano-1-butene-3,3,4-tricarboxylate (5-Bu).** After isomerization of **5-Cb** in DMF, water was added and the product extracted with diethyl ether (colorless oil). Yield: 16%. IR (NaCl neat): 3030 (=C—H str.), 2900, 1735, 1655 (C=C str.), 1615, 1590, 1260, 755, 730 cm^{-1}.

Stereochemistry of *trans*-1-Butenes. Structural isomers of **2-Bu** were assigned by ^{13}C NMR (Table V). C3 and C4 carbons of *trans*-1-butenes are easily distinguishable, because only C4 has a hydrogen (doublet in off-resonance spectrum). C4 of **1-Bu** and **3-Bu**, having two cyano substituents, showed absorptions at 35.69 and 31.12 ppm, respectively. C3 of **1-Bu**, having two cyano groups, appears at 41.28 ppm. In contrast, C4 in **4-Bu-a** and **-b**, having one cyano and one methyl ester, resonates at 45.09 and 44.70 ppm, respectively, and C3 at 50.94 and 50.03 ppm, respectively. Therefore, C4 carbons having two cyano groups should appear above 30 ppm, C4 carbons having one cyano and one methyl ester groups and 45 ppm, C3 carbons having two cyano groups around 40 ppm, and C3 carbons having one cyano and one methyl ester groups around 50 ppm.

The ^{13}C NMR spectrum of **2-Bu** showed C4 at 32.03 ppm and C3 at 52.43 ppm for one structural isomer and C4 at 46.03 and C3 at 38.46 ppm for the other isomer. Therefore, the former is assigned to **2-Bu-a** and the latter to **2-Bu-b**.

1-(Carbazol-9-yl)-1-methoxy-3,3,4,4-tetracyanobutane (1-MeO). Methanol was evaporated after CT color disappeared, and a partially crystalline viscous oil remained, which was recrystallized from a diethyl ether/*n*-hexane mixture (white needles). Yield: 85%. Mp: 148–149.5 °C (turns red). IR (KBr): 2925, 2225, 1122, 1110 (C–O str.), 755, 730 cm^{-1}. MS (10 eV): 353 (M^+), 326 (M^+ - HCN), 294 (M^+ - HCN and CH_3OH, main), 229 (294 - •CH(CN)$_2$), 210, 167 ($NHCZ^{+\bullet}$).

Methyl 1-(Carbazol-9-yl)-1-methoxy-3,4,4-tricyanobutane-3-carboxylate (2-MeO-a) and Methyl 1-(Carbazol-9-yl)-1-methoxy-3,3,4-tricyanobutane-4-carboxylate (2-MeO-b). After evaporation of methanol, crystals were obtained as white needles (recrystallized from dichloromethane/diethyl ether). Yield: 86%. Mp: 176.5–178.0 °C (turns red).

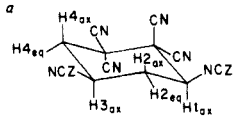
Table XI. ^1H and ^{13}C NMR Data for Cyclohexane **7** in $CDCl_3$[a]

^1H NMR data	
chem shifts δ	coupling const, Hz
$H1_{ax}$ = 6.35	J1ax-2ax = 11.4
$H2_{ax}$ = 3.92	J1ax-2eq = 5.0 (4.7)
$H2_{eq}$ = 3.58	J2ax-2eq = 15.6 (16.2)
$H3_{ax}$ = 5.79	J2ax-3ax = 16.0
$H4_{ax}$ = 3.85	J2eq-3ax = 5.0
$H4_{eq}$ = 3.06	J3ax-4ax = 16.5
aromatic = 7.20–8.21	J3ax-4eq = 5.2
	J4ax-4eq = 15.5 (16.1)

^{13}C NMR chem shifts (ppm) for carbons

C1	C2	C3	C4	C5	C6	CN	aromatic
48.82	34.13	58.94	30.39	41.51	45.75	109.48 109.56 110.35 111.08	109.18~141.26

[a]



IR (KBr): 2925, 1760, 1265, 1130, and 1110 and 1070 (C—O str.), 755, 730 cm^{-1}.

Dimethyl 1-(Carbazol-9-yl)-4,4-dicyano-1-methoxybutane-3,3-dicarboxylate (3-MeO). After evaporation of methanol, colorless viscous oil remained. The oil was washed with *n*-hexane and vacuum dried. Yield: 95%. IR (NaCl neat): 2952, 1740, 1260, 1122 and 1100 (C–O str.), 755, 730 cm^{-1}. MS (5 eV): 419 (M^+), 388 ($M^+ - {}^\bullet OCH_3$), 322 ($M^+ - CH_3OH$ and $^\bullet CH(CN)_2$), 291, 262 (322 - CH_3COOH), 253, 210, 193 ($NVCZ^{+\bullet}$), 188, 167 ($NHCZ^{+\bullet}$, main). Anal. Calcd. for $C_{23}H_{21}N_3O_5$: C, 65.86; H, 5.05; N, 10.02. Found: C, 65.66; H, 5.11; N, 9.97.

Dimethyl 1-(Carbazol-9-yl)-3,4-dicyano-1-methoxybutane-3,4-dicarboxylate (4-MeO). After reaction, methanol was evaporated to give a partially crystalline colorless oil, which was recrystallized from dichloromethane/diethyl ether/*n*-hexane at −50 °C (white crystals). Yield: 95%. Mp: 153–154.5 °C. IR (KBr): 2950, 1755, 1330, 1255, 1125 and 1095 (C–O str.), 1060, 755, 730 cm^{-1}. MS (5 eV): 419 (M^+, main), 392 (M^+ - HCN), 388 ($M^+ - {}^\bullet OCH_3$), 360 ($M^+ - {}^\bullet COOCH_3$), 253, 210, 167 ($NHCZ^{+\bullet}$).

Trimethyl 1-(Carbazol-9-yl)-4-cyano-1-methoxybutane-3,3,4-tricarboxylate (5-MeO). The reaction of **5**-Cb in methanol gave white crystals after evaporation. This was a mixturre of **5**-Cb and **5**-MeO, and pure **5**-MeO was obtained after fractional crystallization of **5**-Cb from dichloromethane/diethyl ether. Yield: 44%. Mp: 153–154 °C. IR (KBr): 2970, 1745, 1260, 1150 and 1105 and 1085 (C–O str.), 755, 730 cm^{-1}. MS (5 eV): 452 (M^+), 421 ($M^+ - {}^\bullet OCH_3$), 322 ($M^+ - CH_3OH$ and $^\bullet CH(CN)(COOCH_3)$), 286 ($M^+ - {}^\bullet NCZ$, main), 167 ($NHCZ^{+\bullet}$). Anal. Calcd for $C_{23}H_{20}N_2O_6$: C, 63.71; H, 5.35; N, 6.19. Found: C, 62.45; H, 5.41; N, 5.97.

Tetramethyl 1-(Carbazol-9-yl)-1-methoxybutane-3,3,4,4-tetracarboxylate (6-MeO). Methanol was evaporated after the reaction, giving white solid containing **6**-MeO and **6**-Cb and parent olefins. The latter materials were separated by recrystallization in dichloromethane/diethyl ether. The residue was recrystallized from *n*-hexane with a small amount of diethyl ether at −50° C (white powdery crystals). Yield: 6%. Mp: 37.5–39.0 °C. IR (KBr): 2965, 1745, 1260, 1160 and 1110 and 1060 (C–O) str.), 755, 730 cm^{-1}. MS (5 eV): 485 (M^+), 453 ($M^+ - CH_3OH$, main), 418, 394 ($M^+ - CH_3COOH$ and $^\bullet OCH_3$), 319 ($M^+ - {}^\bullet NCZ$), 233, 230.

1,3-Di(carbazol-9-yl)-5,5,6,6-tetracyanocyclohexane (7). To a dichloromethane solution (100 mL) of **1** (128 mg, 1 mmol), NVCZ (1.93 g, 10 mmol) was added at once under argon atmosphere. An intense blue-to-violet CT color was observed which faded within 2 min. However, a faint color remained for a couple of hours. After 48 h at room temperature, the solution became slightly yellow. At this period, SEC analysis showed that the solution contained only **7** and polymer. Diethyl ether (400 mL) was slowly added to the reaction mixture, and the precipitated polymer was filtered off. The filtrate was evaporated under reduced pressure at room temperature. A yellow oil was obtained and recrystallized from chloroform–diethyl ether (1:1 v/v) at −10 °C. Yield: 84%. Two successive recrystallization gave colorless crystals. **7** could also be obtained from NVCZ and **1**-Cb. MP: >120 °C (dec (turns red). IR (KBr): 3064 (=C—H str.), 2957 (C—H str.), 2251 (CN), 1624 and 1598 (ring C=C str.), 1484 and 1454 (CH and CH_2 def.), 1329, 1312, 1219, 1163, 1127, 909, 748 and 723 (aromatic ring) cm^{-1}. Anal. Calcd for $C_{34}H_{22}N_6$; C, 79.36; H, 4.31; N, 16.33. Found: C, 79.6; H, 4.50; N, 15.84.

For ^1H and ^{13}C NMR spectral data, see Table XI.

Ultraviolet Measurements of EDA Complexes in Polymerization. The decay of the absorbance at 610 nm in the NVCZ–TCNE–**1** reaction was measured in the following conditions: [**1**] = 0.01 M, [NVCZ] = 0.22 M in dichloromethane at 30.5 °C (1-mm cell). After 30 s, the absorbance has decayed to a minimal constant value.

The decay of absorbance at 440 nm in the NVCZ–**3** reaction was measured in the following conditions: [**3**] = 0.10 M, [NVCZ] = 0.40 M in dichloromethane at 30.5 °C (1-mm cell). After 40 min, the absorbance reached zero.

Comments on the Polymerization NVCZ with 1-Cb. All the following products were checked for their initiating ability. Cyclohexane **7** has weak initiating ability: 5% yield of polymer after 4 h. **7** was also dissolved in methanol, and the solution was left for 48 h at 30 °C. The solution turned red, but methanolysis did not occur at any extent. The polymer formed in NVCZ-**1**-Cb system, purified and put into NVCZ solution, had no initiating ability.

Additive effects were examined in the NVCZ–**1**-Cb system in order to characterize the reaction. 1,4-Dinitrobenzene, a radical inhibitor of medium strength, scarcely affected formation of **7** or polymerization. 1,4-Diazabicyclo[2.2.2]octane (Dabco), a strong cationic inhibitor, quenched the polymerization almost completely. It even reacts with **7** once formed.

Comments on the Polymerization of NVCZ with 3-Cb. 3-Bu and the polymer have no initiating abilities. The effect of additives was also examined in the NVCZ–**3**-Cb system. Addition of 1,4-dinitrobenzene had no effect, while Dabco completely quenched the polymerization.

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Registry No. 1, 670-54-2; **1-MeO**, 102852-11-9; **1-Cb**, 26850-72-6; **1-Bu**, 102852-37-9; **1** (*N,N*-dimethylaniline EDA complex), 13070-99-0; **1** (*N*-ethylcarbazole EDA complex), 20586-55-4; **1** (hexamethylbenzene EDA complex), 2605-01-8; **2**, 101342-43-2; **2-MeO-a**, 102852-12-0; **2-MeO-b**, 102852-13-1; **2-cb-a**, 102852-31-3; **2-Cb-b**, 102852-32-4; **2-Cb-c**, 102852-33-5; **2-Cb-d**, 102852-34-6; **2-Bu-a**, 102852-38-0; **2-Bu-b**, 102852-39-1; **2** (*N,N*-dimethylanaline EDA complex), 102852-18-6; **2** (*N*-ethylcarbazole EDA complex), 102852-23-3; **2** (hexamethylbenzene EDA complex), 102869-68-1; **3**, 82849-49-8; **3-MeO**, 102852-14-2; **3-Cb**, 96735-89-6; **3-Bu**, 102852-40-4; **3** (*N,N*-dimethylaniline EDA complex), 102869-67-0; **3** (*N*-ethylcarbazole EDA complex), 102852-24-4; **3** (hexamethylbenzene EDA complex), 102852-28-8; **4Z**, 101342-44-3; **4E**, 35234-87-8; **4-MeO**, 102852-15-3; **4-Cb-a**, 102852-35-7; **4-Cb-b**, 102918-81-0; **4-Cb-c**, 102918-82-1; **4-Cb-d**, 102918-83-2; **4-Bu-a**, 102852-41-5; **4-Bu-b**, 102852-42-6; **4Z** (*N,N*-dimethylaniline EDA complex), 102852-19-7; **4E** (*N,N*-dimethylaniline EDA complex), 102852-20-0; 4*Z* (*N*-ethylcarbazole EDA complex), 102852-25-5; **4E** (*N*-ethylcarbazole EDA complex), 102852-26-6; **4Z** (hexamethylbenzene EDA complex), 102852-29-9; **4E** (hexamethylbenzene EDA complex), 102852-30-2; **5**, 87040-06-0; **5-MeO**, 102852-16-4; **5-Cb**, 102852-36-8; **5-Bu**, 102852-43-7; **5** (*N,N*-dimethylaniline EDA complex), 102852-21-1; **5** (*N*-ethylcarbazole EDA complex), 102852-27-7; **5** (hexamethylbenzene EDA complex), 102869-69-2; **6**, 1733-15-9; **6-MeO**, 102852-17-5; **6-Cb**, 70839-10-0; **6** (*N,N*-dimethylaniline EDA complex), 102852-22-2; **7**, 102869-66-9; NVCZ, 1484-13-5; NVCZ (homopolymer), 25067-59-8; Dabco, 280-57-9; methanol, 67-56-1; dimethyl ketomalonate, 3298-40-6; methyl cyanoacetate, 105-34-0; malonitrile, 109-77-3.