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^{13}C NMR Studies of the Stereochemistry of 1,2-Poly(cyclobutene-1-carbonitrile) and Related Oligomers

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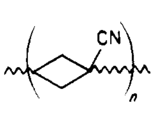
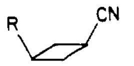
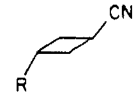
ABSTRACT: ^{13}C NMR studies were performed for a number of related oligomers to understand better the stereochemistry of 1,2-poly(cyclobutene-1-carbonitrile) (PCBC). Additivity relationships, which were based on the dimers, gave empirically calculated ^{13}C chemical shift data that were in good agreement with the data for available trimers. The experimental and calculated chemical shift data for the trimers were used to assign the resonances that occur in the ^{13}C NMR spectrum of PCBC. Although the polymer spectrum is quite complicated, the methine resonances of the cyclobutane rings give two groups of resonances, which are separated by several parts per million depending on the type of ring fusion. From the integrated intensities it is estimated that about 60% of the rings in PCBC are trans fused.

Introduction

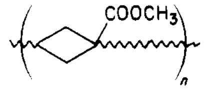
There have been relatively few studies of the stereochemistry of polymers having all rings in the backbone.[1-3] In an NMR study[4] of 1,3-poly(bicyclobutane-1-carbonitrile) (PBBC) and related oligomers **1a** and **1b**, it was shown that

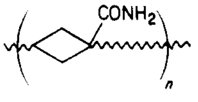

PBBC


1a


1b

substituents R at C3 led to ^{13}C NMR shifts in **1a** that were 1–1.5 ppm upfield of those for the trans isomers **1b**. It was concluded that the nitrile shift provides an important probe of stereochemistry and can be used to investigate the ratio of cis/trans ring enchainments depending on the method of polymer initiation. In a subsequent study of PBBC, 1,3-poly(1-methoxycarbonyl)bicyclobutane) (PMCB), and 1,3-poly(bicyclobutane-1-carboxamide) (PBCA),[5] which were obtained under conditions of better


PMCB


PBCA

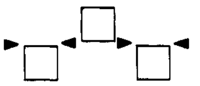
resolution and the use of assignments based on pseudo-INEPT[6] (APT[7]) experiments, polymer sequence distributions were determined; the substituent carbons and the C3 ring carbons exhibit triad structure. The C1 ring carbons in PMCB, for example, exhibit an eight-resonance pentad structure, which is in somewhat better conformity with the first order Markov statistics than Bernoulli statistics. From the ratios of the integrated intensities in the substituent and ring carbon resonances it was shown that the proportions of cis to trans ring enchainments could be ascertained.

Table I
Carbon-13 Chemical Shifts of Cyclobutanecarbonitrile 2 and the Dimers 3a and 3b[a]

	2		**3a**		**3b**	
	$CDCl_3$[b]	Me_2SO[b]	$CDCl_3$	Me_2SO	$CDCl_3$	Me_2SO
δ_1	22.01	20.84	37.30	36.59	39.01	37.71
δ_2	26.95	26.19	30.22[c]	29.78[c]	30.01[c]	28.45[c]
δ_3	19.83	19.23	16.67	16.05	16.50	15.99
δ_4	26.95	26.19	30.04[c]	29.21[c]	29.56[c]	28.32[c]
$\delta_{CN(C_1)}$	122.45	122.70	122.99	123.19	122.04	122.56
$\delta_{1'}$			24.20	22.97	24.17	22.82
$\delta_{2'}$			41.87	40.60	45.53	43.84
$\delta_{3'}$			21.98[d]	21.38[d]	22.26[d]	21.50[d]
$\delta_{4'}$			22.57[d]	21.76[d]	22.40[d]	21.62[d]
$\delta_{CN(C_{1'})}$			119.57	120.29	120.77	121.25

[a] In parts per million downfield of internal $(CH_3)_4Si$; digital resolution: 0.03 ppm. [b] These values were measured in dilute solutions (~10 mg/mL) of 2 in chloroform-*d* and Me_2SO-d_6 because concentration-dependent effects lead to differences of ca. 0.3 ppm for the C_2 and C_4 carbons. However, the ^{13}C chemical shifts of the nitrile groups are within the experimental error in dilute and concentrated solutions. [c,d] The chemical shift assignments in these columns may be reversed.

Another class of polymers containing only cyclobutane rings in the backbone is that based on the polymerization of cyclobutene-1-carbonitrile under free radical conditions[8] leading to the high molecular weight polymer 1,2-poly(cyclobutene-1-carbonitrile) (PCBC). The ^{13}C NMR spectrum of PCBC is more complicated than that of PBBC, PMCB, and PBCA. The dimers and oligomers, which are associated with PCBC, were synthesized and investigated via ^{13}C NMR techniques to understand better the stereochemistry of PCBC. It appears that the only previous study of polymers of this type was performed by Natta and co-workers[2]. In the stereospecific polymerization of cyclobutene they obtained four different polymers. Two of these were thought to be the cis-fused polycyclobutenes (type I and type II), but definitive structural data were not presented.


type I


type II

Results and Discussion

The ^{13}C NMR spectrum of free radical initiated PCBC,[8,9] which was recorded at 62.90 MHz in Me_2SO-d_6 solvent is depicted in Figure 1. The resolution-enhanced nitrile region, which is expanded vertically and horizontally in Figure 1, comprises about eight resonances in the range 120–122 ppm. In contrast to the ^{13}C NMR spectrum of PBBC[4,5] there is not a clear separation between the PCBC nitrile resonances of PCBC, so that it may be necessary to use the ring carbon resonances to distinguish the cis- and trans-fused rings. The methine (C2) resonances in Figure 1 occur downfield of the strong Me_2SO-d_6 resonances, whereas the quaternary (C1), methylene (C3), and methylene (C4) resonances occur at increasingly higher field. The polymer (and oligomer) assignments were verified by a pseudo-INEPT experiment.[6,7]

The syntheses and separation procedures for the oligomers of PCBC are given in the Experimental Section. The ^{13}C NMR chemical shifts of cyclobutane-1-carbonitrile

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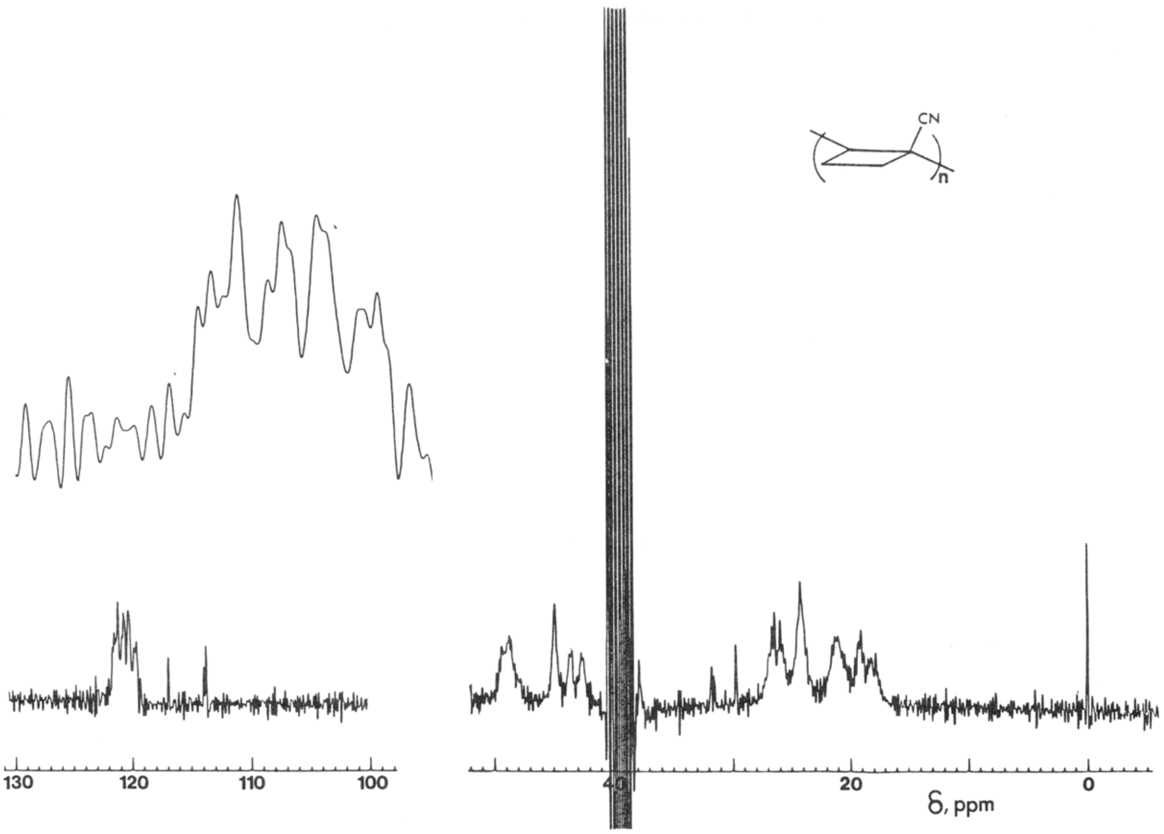
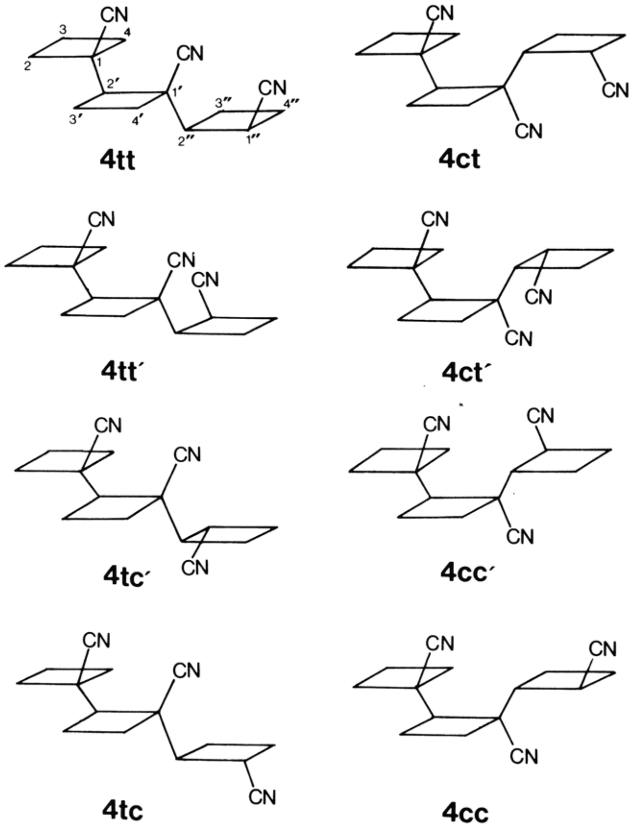
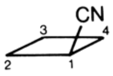


Figure 1. Carbon-13 NMR spectrum of 1,2-poly(cyclobutene-1-carbonitrile) (PCBC). The nitrile region, 119–123 ppm, is expanded in the upper left-hand side of the figure.

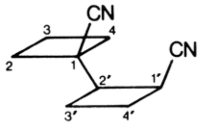
Chart I



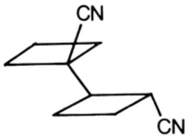
(2) and the dimers *cis*- and *trans*-2-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (**3a**) and (**3b**), respectively, are



2



3a

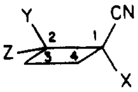


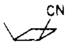
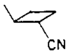
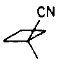
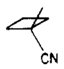
3b

given in Table I. These were measured in both chloroform-*d* and Me_2SO-d_6 solvents. The chemical shifts for **2** are slightly different from those reported previously[4] because they were measured in quite dilute solutions to conform with the lower concentrations of the various oligomers studied here. The chemical shift of the nitrile group at C1 in the cis isomer **3a** is about 1 ppm upfield of that for the trans isomer **3b**. This suggested that the nitrile group was a possible probe of cis/trans stereochemistry in the 1,2-fused polymer as well as the 1,3-fused PBBC.[4,5] The appearance of a single resonance near 123 ppm in all of the oligomers (but not PCBC in Figure 1) provides evidence that this conforms to the nitrile at the terminal (end group) ring. As in previous studies the trans isomer **3b** has greater volatility than the cis isomer, as expected on the basis of lower polarity of the former.

The greater complexity of the oligomers as well as PBBC can be seen upon drawing the structural formulas of eight trimers **4tt**–**4cc′** (Chart I). The notation conforms to that which was used to investigate sequences distributions in the 1-substituted 1,3-poly(bicyclobutenes).[5] Rotation about the bonds connecting the rings can take place, yielding formulas analogous to the type II polycyclobutane proposed by Natta and co-workers.[2] However, space-filling models of the trimers indicate that the nitrile substituents would produce strain that would make these conformations

Table II
Additivity Increments $\Delta\delta_i$ on Introducing Substituents X, Y, and Z into the Cyclobutanecarbonitrile Moiety[a]



X	Y	Z	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_{CN}$
	H	H	15.29	3.27	-3.16	3.09	0.54
			(15.75)	(3.59)	(-3.18)	(3.02)	(0.49)
	H	H	17.00	3.06	-3.33	2.61	-0.41
			(16.87)	(2.26)	(-3.24)	(2.13)	(-0.14)
H		H	2.19	14.92	2.15	-4.38	-2.88
			(2.13)	(14.41)	(2.15)	(-4.43)	(-2.41)
H	H		2.16	18.58	2.43	-4.55	-1.68
			(1.98)	(17.65)	(2.27)	(-4.57)	(-1.45)

[a] In ppm; values in parentheses are based on the compounds measured in Me_2SO-d_6.

Table III
Comparison of the Experimental ^{13}C NMR Data of the Three Trimers in Chloroform-*d* with the Empirically Calculated Data[a]

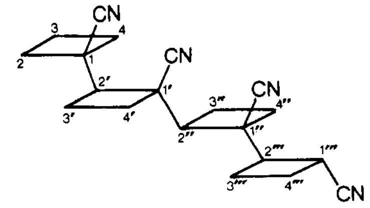
	4tt (4tt′)[b]		4tc		4tc′	
	exptal	calcd	exptal	calcd	exptal	calcd
δ_1	36.60	37.30	37.26	37.30	37.13	37.30
δ_2	30.26	30.22	30.53	30.22	30.20	30.22
δ_3	17.22	16.67	16.60	16.67	16.78	16.67
δ_4	28.82	30.04	30.35	30.04	29.81	30.04
$\delta_{CN(C1)}$	123.59	122.99	122.92	122.99	123.08	122.99
$\delta_{1'}$	40.47	39.49	41.15	41.20	41.96	41.20
$\delta_{2'}$	44.46	45.14 (44.96)	46.31	44.93	46.64	44.48
$\delta_{3'}$	20.20	18.82	18.88	18.65	19.06	18.65
$\delta_{4'}$	25.52	25.66 (25.84)	26.51	25.18	26.37	25.63
$\delta_{CN(C1')}$	120.11	120.11	119.17	119.16	119.34	119.16
$\delta_{1''}$	25.09	24.20	24.24	24.17	23.82	24.17
$\delta_{2''}$	40.72	41.87	46.48	45.53	47.47	45.53
$\delta_{3''}$	21.76	21.98	22.15	22.26	22.28	22.26
$\delta_{4''}$	22.27	22.57	22.15	22.40	23.07	22.40
$\delta_{CN(C1'')}$	120.04	119.57	120.62	120.77	120.56	120.77
σ_s[c]	0.0055		0.0037		0.0054	
σ_i[c]	0.3354		0.2265		0.3272	
r[d]	0.9998		0.9999		0.9998	

[a] All values in ppm downfield of internal $(CH_3)_4Si$; digital resolution 0.03 ppm. [b] Values in parentheses correspond to calculated values for **4tt′**, which differ from those for **4tt**. [c] Standard deviations in slope and intercept. [d] Correlation coefficient of least-squares analysis.

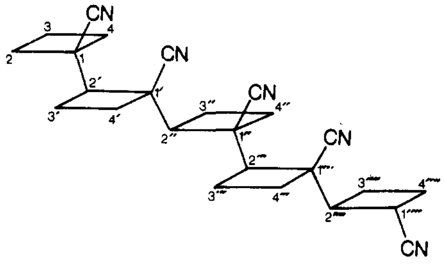
unfavorable. In the absence of experimental data to confirm this, the spectra of the oligomers and the polymer may be averages of several conformations. Therefore, structural formulas of the stereoisomers, which would not be differentiated in the NMR spectra, are not included.

Entered in Table II are the changes $\Delta\delta_i$ due to introducing substituents X, Y, and Z into the cyclobutane-1-carbonitrile moiety. These were obtained from the experimental chemical shift data for **2**, **3a**, and **3b** in Table I. Unfortunately, in the process of separating this series of oligomers, only three trimers, one tetramer, and one pentamer were eluted from the silica gel columns. Calculated results for the trimer chemical shifts, which were based on the "monomer" and dimer data in Table II, are given in Table III. From this table it is noted that one pair can be assigned as **4tc**/**4tc′** because of the agreement between the calculated chemical shifts and the experimental ones that were measured in $CDCl_3$ and also included in Table III; the correlation coefficients in the least-squares fits are at least 0.9998. Of particular importance is the agreement (≤0.6 ppm) between the empirically calculated and experimental shifts of the nitrile groups. On the basis of the agreement between the experimental results and the empirically calculated data, the third trimer in Table III is assigned as **4tt** or **4tt′**, the other possibilities giving correlations that are not as good. Since the ^{13}C NMR spectrum of the polymer was measured in Me_2SO-d_6, for purposes of comparison of chemical shifts, spectra of the three trimers were also obtained in this solvent. The data are given in Table IV. From the additivity data in Table II, the chemical shifts for all eight trimers were calculated and entered in Table IV. From the chemical shift data for the R′ moieties in the trimers RR′R″ in Table IV it appears that only the C2′ carbons of PCBC would be expected to fall into the well-separated bands; the trans ring enchainments should have C2 resonances in the range 43.8–44.7 ppm while cis ring enchainments showed their resonances shifted about 3 ppm downfield.

In the process of separating the oligomers, one tetramer and one pentamer were obtained. Their chemical shifts, measured in chloroform-*d*, are given in Table V. It seems likely that these would conform to extensions of one of the three trimers in Table III. Best agreement of the trimer–tetramer–pentamer data is obtained if it is assumed that the tetramer and the pentamer are **5ttc** and **6tttc**,



5ttc



6tttc

respectively. Evidence for this is based on the experimental data for the trimers ($R_{tr}R_{tr}'R_{tr}''$) in Table III. With notation of the tetramer **5tttc** as ($R_{te}R_{te}'R_{te}''R_{te}'''$), experimental chemical shift data from the trimers are associated as follows: from **4tc**, $R_{tr}'' \rightarrow R_{te}'''$, $R_{tr}' \rightarrow R_{te}''$; from **4tt**, $R_{tr}' \rightarrow R_{te}'$, $R_{tr} \rightarrow R_{te}$. These comparison chemical shift values are included in the third column of Table V. The correlation coefficient between these and the experimental ones in the least-squares analysis is 0.99995. This agreement provides some confidence in the assignment of the tetramer as **5ttc**. Similarly, with notation of the pentamer by ($R_pR_p'R_p''R_p'''R_p''''$), the comparison ^{13}C chemical shift values in Table V were taken directly from the experimental data for the tetramer with the following associations: $R_{te}''' \rightarrow R_p''$, $R_{te}'' \rightarrow R_p'''$, $R_{te}' \rightarrow R_p''$, R_p', and $R_{te} \rightarrow R_p$. In this case the correlation coefficient in the least-squares analysis is 0.9998.

It is unfortunate that we were not able to grow crystals of any of the oligomers for X-ray crystallographic study, as this would have provided an unambiguous verification of these assignments. In any event, it appears that the ^{13}C NMR assignments offer potential as a probe of the stereochemistry in these systems. The identification of trimers, tetramers, etc., is unambiguous as can be seen from representative ^{13}C NMR spectra, measured in chloroform-*d*, and reproduced in Figure 2. In addition to a simple count of the nitriles, the patterns for the ring carbons are straightforward: methylene carbons occur in the range 17–31 ppm, quaternary carbons appear between 36–43 ppm, and the methines are in the range 44–48 ppm. These are also the ranges in which the various resonances occur in Figure 1 for PCBC dissolved in Me_2SO-d_6.

The analysis of the sequence distributions in PCBC is not straightforward as in the 1-substituted 1,3-poly(bicyclobutanes).[5] Data for the eight trimers in Table IV indicate that the methine (C2) carbons in the cis-fused rings should be several parts per million downfield of the trans-fused rings. Therefore, it is resonable to assume that the PCBC methine (C2) carbon resonances in the range 42–46 and 48–50 ppm in Figure 1 arise from trans and cis ring enchainments, respectively. From the integrated intensities it is estimated that the ratio of trans to cis fusions is about 3:2. There are at least eight nitrile resonances in PCBC, but they are not as clearly assignable to the cis and trans fusions as they are in 1,3-poly(bicyclobutane-1-carbonitrile).[5] Moreover, there is insufficient data to sort out the structure of the methylene resonances of PCBC in Figure 1.

Conclusions

The ^{13}C NMR spectra of the oligomers associated with 1,2-poly(cyclobutene-1-carbonitrile) exhibit patterns for the nitrile and ring resonances that are consistent with those of the polymer. The nitrile resonances are not as clearly separated as in the analogous 1,3-fused polymer[5] and are not, therefore, as useful in the determination of the stereochemistry of the polymer. However, the methine (C2) ring carbon resonances are clearly separated into two groups, which can be associated with cis- and trans-fused rings. A somewhat larger fraction (60%) of trans-fused rings is typical of the values observed in the polymers having 1,3-fused cyclobutane rings in the backbone.[4,5]

Experimental Section

Spectra. All carbon-13 spectra were obtained in 10-mm sample tubes at 62.90 MHz on a Bruker Instruments WM-250 superconducting NMR spectrometer using Me_4Si (tetramethylsilane) as internal standard. All spectra have a spectral width of 10000 Hz collected into 16K data points. For the pseudo-INEPT[6] or attached proton test (APT)[7] experiment, the evolution time between 90° and 180° pulses was taken to be 0.0076 s.

Proton spectra were obtained on a Varian Associates T-60 NMR spectrometer. Infrared spectra were taken on a Perkin-Elmer 983 spectrometer between two potassium bromide plates. Elemental analyses were performed by Mic Anal Inc, Tucson, AZ.

Syntheses. 1,2-Poly(cyclobutene-1-carbonitrile) (PCBC). This polymer was prepared under free radical conditions as described by Gale and co-workers.[8]

Cyclobutane-1-carbonitrile. This compound was obtained from Ash Stevens, Inc, Detroit Research Park, Detroit, MI, and was distilled before NMR measurements.

Cyclobutene-1-carbonitrile. The literature method[8,9] of synthesizing this compound was followed. A 60-cm-long quartz column with 3-cm inner diameter was packed with 35 cm of Ascarite (from Aldrich Chemical Co). The temperature of the column was kept at 200 °C for 1 h while nitrogen gas was flowing through it. An addition funnel containing *cis*- and *trans*-dicyanocyclobutane (Chemical Procurement Lab, College Point, NY) was attached to the top of the column. While the temperature was adjusted to 225 °C and pressure to 2 torr, dicyanocyclobutane, which was melted with a heat gun, was added into the column dropwise. The products were collected into two consecutive traps cooled with dry ice and acetone at the bottom end of the column. The water in the product mixture was removed with $MgSO_4$, and the cyclobutene-1-carbonitrile obtained (45–60%) was assumed to be pure based on the proton NMR spectra: ^{1}H NMR ($CDCl_3$) δ 6.80 (m 1 H), 2.86 (m 2 H), 2.65 (m 2 H); IR (neat) 2242, 1488, 1275, 1236, 878 cm^{-1}.

(Triphenylmethyl)sodium Solution. A 1-L, three-neck flask was equipped with a magnetic stirrer, a nitrogen inlet, and a gas outlet. The vessel was dried with a heat gun and cooled under nitrogen. Solid sodium (17 g) was cut into small pieces and transferred to the flask. Then 700 mL of the anhydrous ether and 87.5 g of recrystallized triphenylmethyl chloride were added. The mixture was stirred at room temperature under nitrogen for 16 h to give a deep red triphenylmethylsodium solution and sodium chloride. Sodium chloride was allowed to settle down overnight. Two 1-mL portions of the upper solution were taken out and titrated with standard acid. The concentration of the triphenylmethylsodium was 0.332 M.

Cyclobutane-1-carbonitrile Anion. The triphenylmethylsodium (630 mL) was transferred into a dry 1-L, three-neck flask by cannulation. The solution was cooled with an ice/water bath to below 5 °C and 16.26 g (0.20 mol) of distilled cyclobutane-1-carbonitrile was added slowly via syringe into the vigorously stirred solution. The deep red of triphenylmethylsodium faded to a light pink, and cyclobutane-1-carbonitrilesodium, which is orange, precipitated. The solution was allowed to stand for 12 h and the upper solution was removed by cannulation under nitrogen. Then 500 mL of anhydrous ether was added to the remaining precipitate, the solution was stirred for a few minutes and the precipitate was allowed to settle for a period of 8 h. The upper ether solution of triphenylmethane was removed by cannulation. This washing

Table IV
Comparison of the Experimental ^{13}C NMR Chemical Shifts of Three Trimers in Me$_2$SO-d_6 with Those Calculated for the Eight Possible Trimers 4tt–4cc′^{a}

	4tt (4tt′)^b		4tc		4tc′		4ct (4ct′)^b	4cc (4cc′)^b
	exptal	calcd	exptal	calcd	exptal	calcd	calcd	calcd
δ_1	36.48	36.59	36.51	36.59	36.51	36.59	37.71	37.71
δ_2	29.71	29.78	29.59	29.78	29.53	29.78	28.45	28.45
δ_3	16.29	16.05	16.18	16.05	16.18	16.05	15.99	15.99
δ_4	29.38	29.21	29.32	29.21	29.32	29.21	28.32	28.32
$\delta_{\mathrm{CN(C1)}}$	123.33	123.19	123.09	123.19	123.16	123.19	122.56	122.56
$\delta_{1'}$	40.41	38.72	39.73	39.84	40.69	39.84	38.57	39.69
$\delta_{2'}$	43.76	44.19 (43.62)	44.22	42.86	44.69	42.73	47.43 (46.86)	46.10 (45.97)
$\delta_{3'}$	19.53	18.20	18.43	18.14	18.63	18.14	18.32	18.26
$\delta_{4'}$	25.11	24.78 (25.35)	24.75	23.89	25.11	24.02	24.64 (25.21)	23.75 (23.88)
$\delta_{\mathrm{CN(C1')}}$	120.58	120.78	119.81	120.15	119.81	120.15	121.74	121.11
$\delta_{1''}$	23.63	22.97	22.82	22.82	22.64	22.82	22.97	22.82
$\delta_{2''}$	39.95	40.60	44.37	43.84	45.00	43.84	40.60	43.84
$\delta_{3''}$	21.10	21.38	21.17	21.50	21.17	21.50	21.38	21.50
$\delta_{4''}$	21.49	21.76	21.60	21.62	22.03	21.62	21.76	21.62
$\delta_{\mathrm{CN(C1'')}}$	120.28	120.29	120.99	121.25	121.11	121.25	120.29	121.25
$\sigma_s{}^c$	0.0044		0.0032		0.0046			
$\sigma_i{}^c$	0.2666		0.1920		0.2779			
r^d	0.9999		0.9999		0.9999			

^{a} Chemical shifts are downfield from internal Me$_4$Si; digital resolution 0.03 ppm. ^{b} Values in parentheses correspond to the second (indistinguishable) isomer. ^{c} Standard deviations in slope and intercept. ^{d} Correlation coefficient.

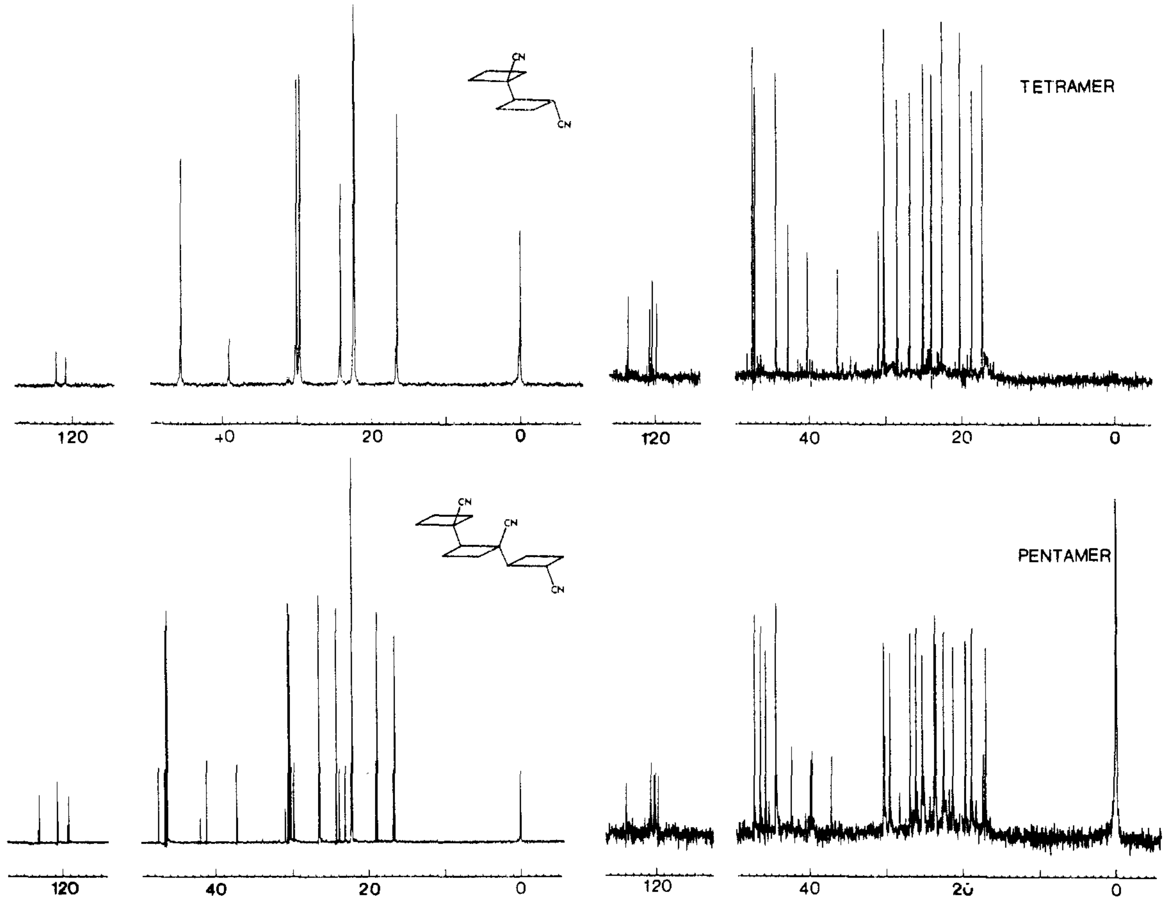


Figure 2. Carbon-13 NMR spectra of the trans dimer, two trimers, tetramers, and pentamers arising from cyclobutene-1-carbonitrile. Of particular interest are the similarities in the groupings for the methylene, quaternary, methine, and CN resonances, which permit unambiguous specification of the number of rings in the oligomers.

process was repeated twice and then freshly distilled tetrahydrofuran (300 mL) was added to the remaining precipitate of cyclobutane-1-carbonitrilesodium, giving a homogeneous pink solution.

Oligomers. With a rapid flow of nitrogen through the system, the apparatus was rearranged to accommodate a dropping funnel (50 mL, equipped with a side arm and a chilling bowl). The reaction vessel was chilled with a dry ice/acetone bath for 20 min. A solution of cyclobutene-1-carbonitrile (10 g) in dry THF (400 mL) was prepared in a 500-mL round-bottom flask. This solution and the dropping funnel were each chilled with a dry ice/acetone bath. With vigorous stirring, the cyclobutene-1-carbonitrile solution was added as a steady stream by cannulation from the 500-mL flask through the chilled dropping funnel into the reaction vessel. The total addition time was about 10 min. The reaction was immediately quenched with 20 mL of propionic acid.

The reaction mixture was then transferred to a 1-L round-bottom flask, concentrated on a rotary evaporator, and redissolved in ether. The salt and polymeric products were filtered out, and the filtrate was concentrated again. Most of the excess of propionic

Table V
Calculated and Experimental ^{13}C Shifts of Tetramer 5 in Chloroform-*d* and Pentamer 6 Compared with the Empirically Calculated Ones[a]

	5ttc		6tttc	
	exptal	comp	exptal	comp
δ_1	36.34	36.60	37.16	36.34
δ_2	30.20	30.26	30.33	30.20
δ_3	17.29	17.22	17.03	17.29
δ_4	28.50	28.82	29.52	28.50
$\delta_{CN(C1)}$	123.47	123.59	123.90	123.47
$\delta_{1'}$	40.21	40.47	39.72	40.21
$\delta_{2'}$	44.31	44.46	44.46	44.31
$\delta_{3'}$	20.20	20.20	21.23	20.20
$\delta_{4'}$	25.03	25.52	26.12	25.03
$\delta_{CN(C1')}$	120.33	120.11	119.75	119.78
$\delta_{1''}$	42.68	41.96	39.90	40.21
$\delta_{2''}$	47.05	46.64	45.77	44.31
$\delta_{3''}$	18.64	19.06	18.87	20.20
$\delta_{4''}$	26.80	26.37	25.30	25.03
$\delta_{CN(C1'')}$	119.78	119.34	120.29	119.78
$\delta_{1'''}$	23.99	23.82	42.36	42.68
$\delta_{2'''}$	47.38	47.47	46.44	47.05
$\delta_{3'''}$	22.55	22.28	19.62	18.64
$\delta_{4'''}$	23.92	23.07	26.90	26.80
$\delta_{CN(C1''')}$	120.65	120.56	120.14	119.78
$\delta_{1''''}$			23.66	23.99
$\delta_{2''''}$			47.28	47.38
$\delta_{3''''}$			22.46	22.55
$\delta_{4''''}$			23.48	23.92
$\delta_{CN(C1'''')}$			120.72	120.65
σ_s[c]	0.0022		0.0036	
σ_i[c]	0.1380		0.2196	
r[d]	0.99995		0.9998	

[a] Chloroform-*d* solvent, chemical shifts in ppm downfield of $(CH_3)_4Si$, other isomers would give a comparable least-squares fit. [b] The comparison values are based on the experimental data for oligomers having one less ring as described in the text. [c] Standard deviations in slope and intercept. [d] Correlation coefficient in least-squares analysis.

acid and cyclubutane-1-carbonitrile was removed by vacuum distillation (50 °C (4 torr)). The remaining crude product was separated by column chromatography.

Separations. The crude product was dissolved in a minimum volume of acetone and applied to a silica gel column (50 cm × 2.5 cm, chromatographic 230-400 silica gel from Sigma) that was wet-packed with eluent (a 15:1 mixture of hexane and acetone). The column was eluted with a hexane/acetone mixture. The ratios and volumes of eluent were 15:1 (1600 mL), 10:1 (2300 mL), 5:1 (1200 mL), 3:1 (400 mL), 2:1 (1200 mL), 1:1 (600 mL). Six hundred 10-mL fractions were collected, and the solvent was evaporated. The constituents of the fractions were examined by NMR (Bruker WM-250).

Trans and Cis Dimers of Cyclobutene-1-carbonitrile. The fractions from no. 54 to no. 98 were found to contain *trans*-2-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (**3b**). This dimer was further purifed with preparative TLC to obtain 320 mg of pure compound: ^{13}C NMR (see Table I); IR (neat) C–H 2993, 2951, 2354, C≡N 2234 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55, N, 17.49. Found: C, 74.32; H, 7.65; N, 16.98.

The fractions from no. 171 to no. 220 contained another dimer, *cis*-2-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile, (**3a**). Further purification by preparative TLC gave 100 mg of pure compound: ^{13}C NMR (see Table I); IR (neat) C–H 2948, 2868, C≡N 2233 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N 17.49. Found: C, 74.31; H, 7.60; N, 17.24.

Trimers. The fractions from no. 251 to no. 330 contained two trimers. Further purification by preparative TLC gave 350 mg of a mixture of 3:1 ratio of two trimers. The carbon-13 NMR spectrum suggested that they were two isomers of 2-[2-(1-cyanocyclobutyl)-1-cyanocyclobutyl]cyclobutane-1-carbonitrile **4tc** and **4tc′**. The fractions from no. 331 to no. 400 gave 147.6 mg of product; further purification by preparative TLC gave 20 mg of the third trimer: IR (Me_2SO) C–H 2993, 2953, 2875, C≡N 2233, 2186 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16; N, 17.56. Found: C, 73.87; H, 6.99; N, 16.79.

Tetramers and Pentamers. One tetramer was found in the fractions from no. 401 to no. 440. The ^{13}C NMR spectrum is shown in Figure 2.

The fractions from no. 458 to no. 600 were a mixture of trimers, tetramers, pentamers, and higher oligomers. These fractions were combined and dissolved in acetone for a second chromatographic separation with a column prepared by the method as described previously. The ratios (volume) of hexane:acetone mixture were 7:1 (2400 mL); 5:1 (600 mL); 4.5:1 (1650 mL); 4:1 (500 mL).

Five hundred 10-mL fractions were collected. These fractions were examined by ^{13}C NMR. It was found that fractions 261–300, 301–330, 331–354, and 355–376 were still mixtures of trimers and tetramers. Only fractions 401–448 yielded about 15 mg of one pentamer after preparative TLC.

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Registry No. **2**, 4426-11-3; **3a**, 100928-85-6; **3b**, 100928-86-7; **4tt**, 100992-54-9; **4tc**, 100928-87-8; **5ttc**, 100928-88-9; **6tttc**, 100928-89-0; PCBC, 25232-93-3; cyclobutene-1-carbonitrile, 23519-88-2; 1,2-dicyanocyclobutane, 3396-17-6.

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