carbinyl chloride. The boiling points were as follows: cyclopropylcarbinyl chloride, 87.5° (lit.[4] bp 87–89°); cyclobutyl chloride, 80.2° (lit.[4] bp 82–83°); and allylcarbinyl chloride, 71.1° (lit.[4] bp 73–74°). Identification was made with their nmr and ir spectra.

Solvents. Solvents of ACS Reagent Grade or Spectroquality Grade were used. They were purified by standard procedures whenever necessary. For the present purpose, the purified solvent was washed several times with distilled water and dried first over anhydrous sodium sulfate and then over activated Type 5A Molecular Sieves for 1 day at −5°. This was distilled with equipment baked at 160° for longer than 24 hr before use. The distillate was stored in a baked bottle with Type 4A Molecular Sieves at −5°.

Aluminum Chloride Solution. A stock solution of r equals 1/10 was prepared by dissolving pulverized aluminum chloride (Matheson Coleman and Bell, ACS Reagent Grade) from a newly opened bottle in nitromethane strictly purified as stated above. A colorless solution was obtained. A gentle stream of dry nitrogen gas was applied to expel the hydrogen chloride gas possibly accumulated in the aluminum chloride bottle before use. It was also applied to substitute nitrogen for the air in the bottle of aluminum chloride stock solution. This solution was stored at −5°. The activity of this solution stayed nearly constant for more than 1 week, proven by the amazingly high reproducibility of kinetic runs, one example of which can be seen in Figure 1a. For reactions above room temperature for which diminished aluminum chloride activity is desired, the aluminum chloride solution was prepared by dissolving a portion of aluminum chloride in nitromethane which was dried over anhydrous sodium sulfate. The water content which is in equilibrium with hydrous sodium sulfate crystals in the bottle effectively diminishes the aluminum chloride activity. After 2 days at room temperature, the activity reached adequate stability for the kinetic study. An initial concentration of 0.1 M was found most adequate.

Kinetic Runs. The aluminum chloride solution and the additional inert solvent were placed in a thermostated reaction bottle with a magnetic stirrer and a thermometer and connected to a dry nitrogen stream. The temperature stability was kept to within 0.1° inside the reaction mixture even at −40°. A solution of the reactant in nitromethane or in the inert solvent was kept at the same temperature and was introduced to the reaction bottle after both reached the desired temperature. A small portion of the reaction mixture was drawn out from time to time with a glass dropper cooled with Dry Ice–acetone under nitrogen gas flow. The reaction mixture was quenched with ice-cold distilled water saturated with n-butyl alcohol which secured the maximum efficiency for both instant quenching and the later analysis of the reaction mixture. Solid anhydrous sodium sulfate was then introduced to break the emulsion and to salt out the portion of organic chloride in the water layer. Analysis of the mixture was made by a Perkin-Elmer Model 226 gas chromatograph with an Infotronic Model CRS-1 chromatograph readout system and a Victor Digit-matic printer. The quenched reaction mixture was kept in an ice bath while waiting for analysis.

The reaction is especially sensitive to moisture and other oxygen-containing organic substances, such as alcohols, ethers, and ketones. No activation effect was observed on the introduction of very small amounts of water as in ordinary Friedel–Crafts and related reactions. The effect is seriously deactivating. Contamination of a metallic ion from a broken magnetic stirrer was found to accelerate the reaction above room temperature, but no systematic study on this problem was carried out. Careful elimination of all possible influencing factors made it possible to bring the reproducibility of the kinetic runs within the range of better than 3% error in the consumption rate constants.

For gas chromatographic analyses, a 150-ft Golay column with either diethylene glycol succinate or Carbowax K1540 was used. The column temperature was kept at 60–70° and the injection temperature 100–150°. These conditions give a reproducibility of analysis of better than ±1% for the main component and ±10% for the minor component of the chloride mixture. That no appreciable change in composition of the solutions took place in the injection block or the column was checked carefully with simulated solutions of known composition.

The kinetic runs in chlorobenzene were carried out as follows. Weighed portions of aluminum chloride were added to the thermostated chlorobenzene with vigorous stirring under dry nitrogen gas. After 10 min, a solution of the reactant in chlorobenzene at the same temperature was introduced and the kinetic run started. The kinetic plot generally shows an unstabilized preequilibrium period of 2–5 min depending on the quantity of aluminum chloride, the temperature, the efficiency of stirring, and other factors. Kinetic data were taken from the later portion of the plot.

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Syntheses and Coordination Ability of Some 1,5-Cyclopolymethylenetetrazoles[1]

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Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received April 12, 1968*

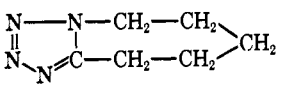
Abstract: A series of 1,5-cyclopolymethylenetetrazoles were synthesized with the hydrocarbon chain containing 3, 4, 6, 7, 8, 9, and 11 methylene groups. The donor properties of these compounds were investigated by spectrophotometric measurements of the tetrazole–iodine charge-transfer complex formation constants in the 5–35° interval. The solvent was 1,2-dichloroethane. The enthalpy and the entropy changes for the complexing reactions were determined from the temperature coefficient of the stability constant. The donor properties of tetrazoles were rather weak and the formation constant values at 25° ranged from 1.42 to 2.64 l. mol^{-1}. There does not seem to be a simple correlation between the length of the hydrocarbon chain and the stability of the iodine complex.

Although the chemical properties of pentamethylenetetrazole (I) have been rather thoroughly studied by a number of investigators, surprisingly the lower homologs of pentamethylenetetrazole have not been investigated to any significant extent. In fact, literature search indicates that there exists only one report on the preparation of tri- and tetramethylenetetrazole (C_3MT and C_4MT, respectively)[3] and another similar

(1) Abstracted from the Ph.D. Dissertation of Frank M. D'Itri, Michigan State University, 1968.

(2) Socony-Mobil Fellow, 1967–1968.

(3) von Kereszty and Wolf, German Patent 611,692; *Chem. Abstr.*, **29**, 5994 (1935); U.S. Patent 2,008,536; *Chem. Abstr.*, **29**, 5604 (1935).



I

report on the corresponding hexa- and heptamethylenetetrazoles (C_6MT and C_7MT, respectively).[4] In both cases, methods of preparation have been only sketchily described.

In recent years physicochemical properties of pentamethylenetetrazoles have been studied quite intensively[5-8] in our laboratories. It has been found that in aqueous solutions C_5MT does not possess any proton affinity, but, on the other hand, in nonaqueous solvents it is capable of forming complexes with Lewis acids such as the halogens and the transition metal ions.

The investigation of the physicochemical properties of 1,5-substituted tetrazoles has been extended in these studies to other polymethylene derivatives. It was of particular interest to us to synthesize compounds with varying numbers of polymethylene groups in the chain, to study their donor properties, and to see whether there is some correlation between the size of the hydrocarbon chain and the complexing ability of the cyclopolymethylenetetrazoles.

Experimental Section

Reagents. Pentamethylenetetrazole used in this investigation was obtained from the Knoll Pharmaceutical Co. under the registered name "Metrazol." It was purified by recrystallization om anhydrous ether and stored over P_2O_5. The melting point of the crystals was 61°. All cyclic ketones were obtained from the Aldrich Chemical Co.; the chloroalkanenitriles were obtained from the Columbia Organic Chemical Co.; sodium azide was Eastman Kodak Yellow Label; and the chlorosulfonic acid came from the Matheson Coleman and Bell Co. All of these chemicals were used without further purification.

4-Azidobutyronitrile. The method outlined by Carpenter[9] was used. A mixture of 4-chlorobutyronitrile (100 g, 1.033 mol), 124 of sodium azide (1.94 mol), and 500 ml of diethylene glycol were stirred in a 1-l., three-necked, round-bottom flask fitted with a stirrer, reflux condenser, and an alcohol thermometer at 100° for 24 hr. The crude product was isolated by steam distillation, and the 4-azidobutyronitrile was separated from the aqueous layer. The aqueous layer was then extracted with three 200-ml portions of ethyl ether for an additional yield of product. The crude product was then dried by filtration through a 3-mm layer of anhydrous sodium sulfate and distilled under reduced pressure, bp 54° (0.25 mm). The final product (75.4 g, 70% yield) was a colorless liquid with a refractive index of 1.4574 at 23.5°.

5-Azidovaleronitrile. Starting with 5-chlorovaleronitrile, this compound was prepared in the manner previously described to prepare 4-azidobutyronitrile. The boiling point was 62° (0.5 mm), and the final product (70.0 g, 57% yield) was a colorless liquid which has a refractive index of 1.4605 at 23.0°.

Hydrazoic Acid. The method outlined by Braun[10] was used to prepare solutions of hydrazoic acid in benzene. Since hydrazoic acid vapors are very toxic, all reactions involving its use were performed in a hood.

Trimethylenetetrazole. von Kereszty's method[3] modified by Carpenter[11] was used for this preparation. A solution of 11.0 g of 4-azidobutyronitrile (0.099 mol) in 100 ml of chloroform, dried over calcium chloride, was added from a dropping funnel to a well-stirred solution of 11.30 g of chlorosulfonic acid (0.097 mol) in 100 ml of chloroform and dried over calcium chloride for 1 hr. The rate of addition was controlled to maintain the temperature of the reaction mixture between 20 and 40°. A white, solid complex precipitated from the solution when the 4-azidobutyronitrile–chloroform solution was added. The mixture was stirred in a flask for 12 additional hr, cooled to 0°, and made basic with 50 ml of 25% aqueous sodium hydroxide solution. Neutralized mixture was stirred for additional 20 min and then the chloroform layer was removed and evaporated to dryness. The crude product was dissolved in 100 ml of water and made acidic with 15 ml of concentrated sulfuric acid, and the unreacted 4-azidobutyronitrile was oxidized with a 0.2 *N* potassium permanganate solution. The trimethylenetetrazole was extracted from the aqueous layer with four 100-ml portions of chloroform. The final purification was accomplished by recrystallizing approximately 10 g of trimethylenetetrazole from a solvent mixture of 50 ml of carbon tetrachloride and 10 ml of ethanol. The distinctive, colorless crystals that were obtained melted at 110° (lit.[3] mp 110°). The yield of trimethylenetetrazole (total 8.18 g) based on 4-azidobutyronitrile was 74%.

Tetramethylenetetrazole was prepared starting with 11.00 g of 5-azidovaleronitrile (0.089 mol) in the manner previously described for the preparation of trimethylenetetrazole. However, an oil formed instead of a white solid precipitate when the 5-azidovaleronitrile–chloroform mixture was added to the chlorosulfonic–chloroform solution. The crude product (6.00 g, 54.5% yield) was purified in the manner described above for trimethylenetetrazole and recrystallized from a carbon tetrachloride–ethanol solvent mixture. The colorless crystals that were obtained melted at 117° (lit.[3] mp 115°). The yield (total 4.80 g) based on 5-azidovaleronitrile was 43.5%.

Hexamethylenetetrazole. A mixture of 12 g of cycloheptanone (0.107 mol) and 20 g of hydrazoic acid (0.466 mol, 188 ml of 2.5 *N* hydrazoic acid–benzene solution) was added to 100 ml of freshly distilled benzene to make a total volume of approximately 300 ml. This mixture was then added over a period of 45 min to a well-stirred, ice-cooled mixture of 60 ml of concentrated sulfuric acid and 100 ml of benzene. After the reaction was completed, ice and water were added to the mixture. Two layers were formed; the aqueous layer was cooled to 0° and neutralized with 50% aqueous sodium hydroxide solution. The crude product (12.0 g, 79.5% yield) was extracted from the aqueous layer with ethyl ether, purified in the manner described for trimethylenetetrazole, and recrystallized from hexane (mp 68°, lit.[4] mp 68°). The yield of the product (total 6.80 g) based on cycloheptanone was 46%.

Heptamethylenetetrazole. Concentrated sulfuric acid (80 ml) was added to an ice-cooled mixture of 20.80 g of hydrazoic acid (0.484 mol, 323 ml of 1.5 *N* hydrazoic acid–benzene solution) in a 1-l., three-necked, round-bottom flask equipped with a mechanical stirrer, dropping funnel, and thermometer. A solution of 20 g of cyclooctanone (0.159 mol) dissolved in 80 ml of benzene was added from a dropping funnel. Then the reaction mixture was stirred for an additional 20 min before the mixture was poured into an ice–water mixture and the two layers were formed. The aqueous layer was cooled to approximately 5° and neutralized with 50% aqueous sodium hydroxide solution. This was followed by three successive extractions with ethyl ether. The benzene layer which contained only a small fraction of the product was also evaporated, and the oily residue was added to the evaporated ethyl ether residue. The recovered crude product (23.90 g, 90.5% yield) was an oil which was purified further by distillation under vacuum. The fraction with a boiling range of 140–150° (0.5 mm) was collected, lit.[4] bp 145–146° (0.1 mm). The oil was difficult to crystallize and seed crystals were first obtained by freezing a small sample at 0° for approximately 30 days. The crystals were then used to induce crystallization of the oil. The product had mp 40–55°. The crude heptamethylenetetrazole (20 g, 0.12 mol) was dissolved in 200 ml of a mixture of equal parts of ethanol and water and was made acidic with 50 ml of concentrated sulfuric acid and enough 0.2 *N* potassium permanganate (about 25 ml) was added to oxidize the azide impurities. The crude product was then extracted with four 100-ml aliquots of chloroform which were evaporated to a yellow oil. A solution of the oil was made at room temperature in 400 ml of ethyl ether, and crystallization of heptamethylenetetrazole was induced when the solution temperature was reduced to approximately −60°. Three or four recrystallizations were required before seeding of the chilled, saturated solution was no longer required. The purified heptamethylenetetrazole was dried *in vacuo*,

(4) L. von Ruzicka, M. W. Goldberg, and M. Hurbin, *Helv. Chim. Acta.*, **16**, 1335 (1933).
(5) A. I. Popov, C. C. Bisi, and M. Craft, *J. Am. Chem. Soc.*, **80**, 6513 (1958).
(6) (a) A. I. Popov and R. D. Holm, *ibid.*, **81**, 3250 (1959); *J. Phys. Chem.*, **66**, 158 (1962).
(7) T. C. Wehman and A. I. Popov, *ibid.*, 70, 3688 (1966).
(8) (a) F. M. D'Itri and A. I. Popov, *Inorg. Chem.*, **5**, 1670 (1966); (b) *ibid.*, **6**, 597 (1967); (c) *ibid.*, **6**, 1591 (1967).
(9) W. R. Carpenter, *J. Org. Chem.*, 27, 2085 (1962).
(10) J. Braun, *Ann.*, **490**, 125 (1931).
(11) W. R. Carpenter, private communication.

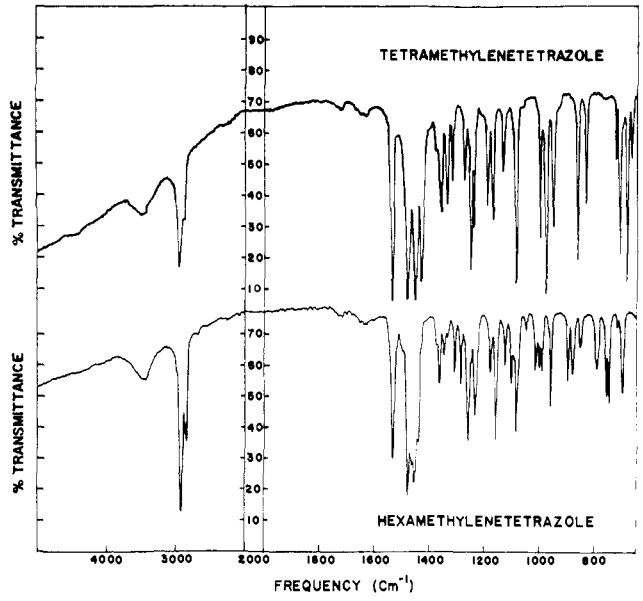


Figure 1. Infrared absorption spectra of tetra- and hexamethylenetetrazole in KBr pellets.

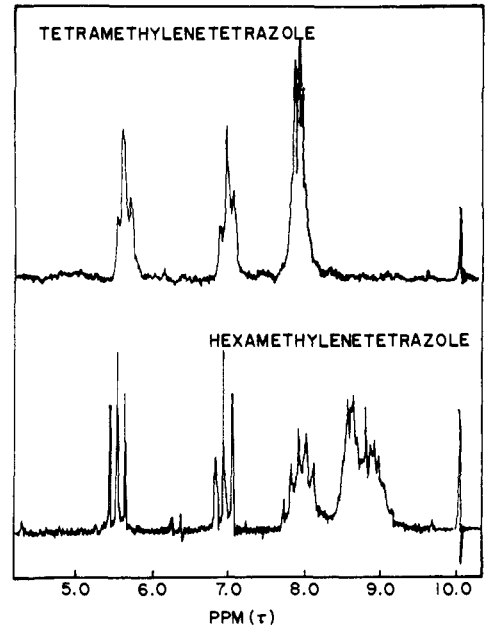


Figure 2. Nuclear magnetic resonance spectra of tetra- and hexamethylenetetrazole in chloroform and carbon tetrachloride, respectively. The samples are calibrated relative to tetramethylsilane used as the internal standard.

and the crystals melted at 42–43°. The yield based on cyclooctanone was 75%. It is interesting to note that the only previously published literature report on this compound[4] describes it as an oil impossible to crystallize.

Octamethylenetetrazole. Starting with 5.5 g of cyclononanone (0.039 mol), this compound was prepared in the manner described for the preparation of heptamethylenetetrazole. The crude product recovered by evaporating the ethyl ether was purified as previously described and then recrystallized from a solvent mixture composed of ethanol:hexane (1:50). The purified octamethylenetetrazole was obtained as colorless crystals and had a melting point of 117–118°. The yield, based on the cyclononanone, was 63.5% (4.8 g).

Nonamethylenetetrazole. Starting with 5.0 g of cyclodecanone (0.031 mol), nonamethylenetetrazole was prepared in the manner described for the preparation of heptamethylenetetrazole. Most of the crude product was recovered from the benzene layer. The aqueous layer, however, was extracted three times with 100-ml portions of ethyl ether in order to recover an additional small fraction of the product. The crude product was recrystallized from a solvent mixture composed of benzene:hexane (1:20). The purified nonamethylenetetrazole was obtained as colorless crystals with a melting point of 90–91°. The yield of the reaction (4.8 g) based on cyclodecanone was 80.0%.

Undecamethylenetetrazole was prepared by adding, from a dropping funnel, a solution composed of 22.0 g of cyclododecanone (0.137 mol) dissolved in 50 ml of dry benzene to a mixture of 20.8 g of hydrazoic acid (0.484 mol, 225 ml of a 2.2 *N* hydrazoic acid–benzene solution) and 80 ml of concentrated sulfuric acid (1.50 mol). The mixture of cyclododecanone was added at a rate adjusted to maintain the reaction mixture temperature at approximately 10° with external cooling. After this addition was complete, the stirring process was continued for 36 hr at 25°. From this point the reaction mixture was treated in the manner described for heptamethylenetetrazole except that benzene instead of ethyl ether was used to extract the product. The crude product was recrystallized three times from a solvent mixture composed of equal parts of water and ethanol. The purified undecamethylenetetrazole was obtained as colorless crystals in a 66.2% yield (20.1 g) based on cyclododecanone and had a melting point of 66–67°. Analytical and physical data for this compound as well as other cyclopolymethylenetetrazoles are given in Table I.

Ir and Nmr Studies. The infrared spectra of the various 1,5-cyclopolymethylenetetrazoles were determined in the 5000–670-cm^{-1} region with a Unicam SP.200 spectrometer in potassium bromide pellets containing approximately 2 mg of compound/300 mg of KBr. The spectra of the various 1,5-cyclopolymethylenetetrazoles compare well with the spectrum of pentamethylenetetrazole except for slight shifts and a variance of intensities of some bands. A sample spectrum of tetra- and hexamethylenetetrazole is given in Figure 1.

The proton magnetic resonance spectra of the cyclopolymethylenetetrazoles are essentially the same with the exception of trimethylenetetrazole which shows a more complex spectrum due to spin–spin splitting. A typical spectrum of the remaining cyclopolymethylenetetrazoles (Figure 2) has two triplet bands with a unit area at about τ 5.5 and 6.9, respectively, and a third or fourth band, depending on the cyclopolymethylenetetrazole, at about τ 8.0 and 8.6, respectively, which are integer values of the first two peaks. The resonance peaks of the various cyclopolymethylenetetrazoles are given in Table II. A sample nmr of tetra- and hexamethylenetetrazole is given in Figure 2.

Purification of 1,2-Dichloroethane. The crude 1,2-dichloroethane (5-l. batches) was washed with 600 ml of a 5% aqueous sodium hydroxide solution and with three 500-ml portions of distilled water. The product was stored over anhydrous calcium chloride for 24 hr. The washed 1,2-dichloroethane was then refluxed over granulated barium oxide for 24 hr and fractionally distilled. The fraction retained had a boiling point of 83.4° (lit.[12] bp 83.5°).

Spectrophotometric Techniques. All measurements were made in stoppered, matched 1-cm silica cells on a Beckman DU spectrophotometer. This instrument was equipped with Beckman thermospacers to control the temperature of the sample compartment. The appropriate temperature was maintained by circulating water from a constant-temperature bath through the thermospacers. By controlling the temperature of the bath, the temperature of the cell compartment was regulated to within ±0.1° for each of the following four temperatures: 5.0, 15.0, 25.0, and 35.0°. Nitrogen circulation was essential during the absorbance measurements at the lower temperatures to prevent moisture condensation. The absorbances of each of the iodine solutions of a given cyclopolymethylenetetrazole were measured at a series of wavelengths near the complex absorption maximum.

Preparation of Solutions. Stock solutions of the cyclopolymethylenetetrazoles and of iodine were prepared by direct weighing of the respective compound into a volumetric flask and dilution to the calibration mark with purified 1,2-dichloroethane at the appropriate temperature.

Spectrophotometric Measurements. The iodine concentrations of these solutions were such ($\approx 10^{-3}$ *M*) that the absorbances in the region of the complex absorption maximum were approximately 0.5 at the respective temperature. Samples of these stock solutions were mixed by volumetric measurement into 25-ml volumetric flasks. The flasks were diluted to the mark with 1,2-dichloroethane which had previously been brought to the desired temperature in

(12) A. I. Vogel, *J. Chem. Soc.*, 644 (1948).

Table I. Analytical and Physical Data of Some Cyclopolymethylenetetrazoles

Trivial name	Mp, °C	Calcd, %			Found, %		
		C	H	N	C	H	N
Trimethylenetetrazole	110	43.63	5.49	50.88	43.74	5.41	51.04
Tetramethylenetetrazole	117	48.37	6.50	45.31	48.46	6.41	45.20
Hexamethylenetetrazole	68	55.24	7.95	36.81	55.32	7.93	36.61
Heptamethylenetetrazole	42–43	57.81	8.49	33.70	57.94	8.47	33.74
Octamethylenetetrazole	117–118	59.97	8.95	31.08	60.09	8.90	31.08
Nonamethylenetetrazole	90–91	61.82	9.34	28.84	61.93	9.31	28.82
Undecamethylenetetrazole	66–67	64.83	9.97	25.20	64.84	9.88	25.23

Table II. The Nmr Absorption Bands of Some Cyclopolymethylenetetrazoles and Some Selected Tetrazoles[a]

Tetrazole	Solvent	Nmr resonance bands			
Trimethylenetetrazole	$CHCl_3$	5.60 VC (1)	6.90 VC (1)		
Tetramethylenetetrazole	$CHCl_3$	5.65 t (1)	7.00 t (1)	7.90 C (2)	
Pentamethylenetetrazole	$CHCl_3$	5.50 t (1)	6.95 t (1)	8.10 C (3)	
Hexamethylenetetrazole	CCl_4	5.45 t (1)	6.85 t (1)	8.05 C (2)	8.55 C (2)
Heptamethylenetetrazole	CCl_4	5.40 t (1)	6.90 t (1)	8.05 C (2)	8.60 C (3)
Octamethylenetetrazole	$CHCl_3$	5.50 t (1)	6.92 t (1)	8.00 C (2)	8.72 C (4)
Nonamethylenetetrazole	$CHCl_3$	5.55 t (1)	6.95 t (1)	8.00 C (2)	8.83 C (5)
Undecamethylenetetrazole	$CHCl_3$	5.55 t (1)	7.00 t (1)	8.00 C (2)	8.68 C (2)
1-Methyltetrazole	DMF	0.68 s (3)	5.70 s (3)		
5-Methyltetrazole	DMF		7.40 s		
1,5-Dimethyltetrazole	$CDCl_3$	5.95 s (1)	7.42 s (1)		

[a] s = singlet, t = triplet, C = complex band, VC = very complex band. The numbers within the parentheses are the respective relative areas. Values were selected from J. H. Markgraf, W. T. Bachmann, and D. P. Hollis, *J. Org. Chem.*, **30**, 3472 (1965).

Table III. Thermodynamic Constants for the Reaction $C_nMT + I_2 \rightleftarrows C_nMT \cdot I_2$ in 1,2-Dichloroethane Solutions at 25°

Temp, °C	K_f, M^{-1}	$\Delta G°$, cal/mol	$\Delta S°$, eu	ΔH, kcal/mol
		Trimethylenetetrazole		
35.0	1.16 ± 0.06	−91	−10.8	−3.4
25.0	1.42 ± 0.09	−215		
15.0	1.63 ± 0.04	−299		
5.0	2.10 ± 0.03	−454		
		Tetramethylenetetrazole		
35.0	1.68 ± 0.06	−318	−15.2	−5.0
25.0	2.34 ± 0.06	−504		
14.8	3.08 ± 0.05	−644		
5.1	4.11 ± 0.22	−782		
		Pentamethylenetetrazole		
35.0	1.69 ± 0.04	−321	−12.3	−4.1
25.0	2.18 ± 0.04	−461		
15.0	2.75 ± 0.04	−579		
5.0	3.46 ± 0.07	−686		
		Hexamethylenetetrazole		
36.0	1.98 ± 0.04	−354	−14.2	−4.7
25.0	2.44 ± 0.05	−529		
15.0	3.14 ± 0.08	−655		
6.5	4.01 ± 0.22	−772		
		Heptamethylenetetrazole		
35.1	2.08 ± 0.05	−446	−11.9	−4.1
25.0	2.64 ± 0.05	−575		
15.1	3.42 ± 0.10	−704		
5.1	4.23 ± 0.08	−797		

the constant-temperature bath. Samples of these solutions were transferred to 1-cm glass-stoppered silica absorption cells and placed in the thermostated cell compartment. The absorbances were measured at 430, 420, 410, and 400 mμ using pure 1,2-dichloroethane in the reference cell.

Spectral data obtained from the cyclopolymethylenetetrazole–iodine mixtures were used to calculate the formation constant of the complex using the method described by Ketelaar, *et al.*[13]

(13) J. A. A. Ketelaar, C. van deStolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952).

In the Ketelaar equation ϵ_t is the apparent molar absorptivity of

$$\frac{1}{\epsilon_t - \epsilon_{I_2}} = \frac{1}{C_D} \frac{1}{K_f(\epsilon_c - \epsilon_{I_2})} + \frac{1}{\epsilon_c - \epsilon_{I_2}}$$

iodine (*i.e.*, the measured absorbance of the solution divided by the total iodine concentration), ϵ_c and ϵ_{I_2} are the molar absorptivities of the complex and iodine, respectively, K_f is the formation constant of the complex, and C_D is the total concentration of the respective cyclopolymethylenetetrazole. A plot of $1/(\epsilon_t - \epsilon_{I_2})$ *vs.* $1/C_D$ should produce a straight line. From the slope and intercept of this

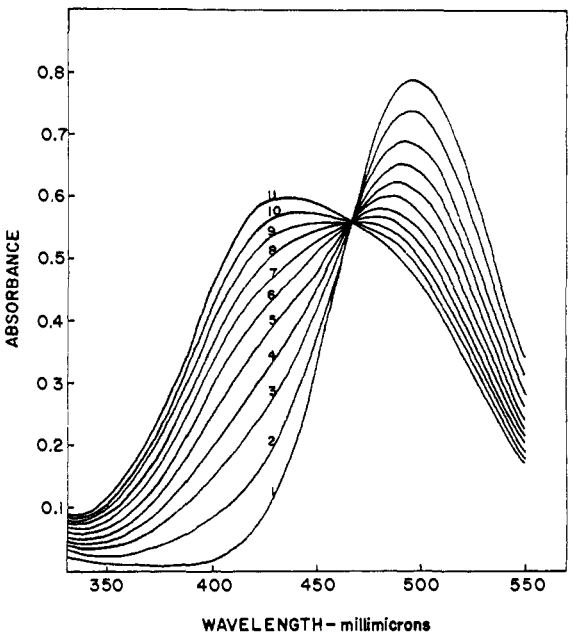


Figure 3. Absorption spectra of tetramethylenetetrazole–iodine system in 1,2-dichloroethane solutions: $C_{I_2} = 8.89 \times 10^{-4}$ *M*; C_{C_4MT} (*M*) (1) 0.00, (2) 0.042, (3) 0.084, (4) 0.126, (5) 0.168, (6) 0.210, (7) 0.252, (8) 0.294, (9) 0.337, (10) 0.379, (11) 0.425.

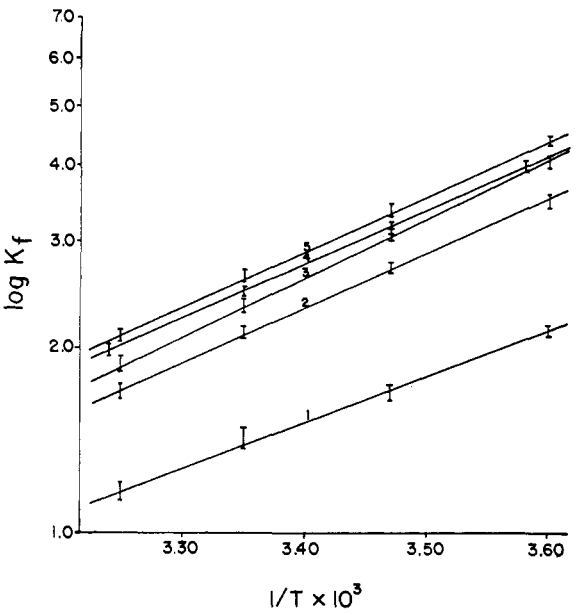


Figure 4. The relations between log K_f and $1/T$ for (1) trimethylenetetrazole, (2) pentamethylenetetrazole, (3) tetramethylenetetrazole, (4) hexamethylenetetrazole, and (5) heptamethylenetetrazole.

line, the formation constant and the molar absorptivity of the complex can be determined.

Once the formation constants for the respective cyclopolymethylenetetrazole–iodine complexes are known at several different temperatures, they may be used to calculate the free energy, enthalpy, and entropy of the complex-forming reaction from the temperature dependence of K_f.

For these measurements it is important to have the cyclopolymethylenetetrazoles in high degree of purity because very small amounts of residual starting material (azide ion or the respective azidoalkanenitrile) will reduce equivalent amounts of iodine to iodide ion, which reacting with excess iodine will form the triiodide ion. The presence of triiodide ion is evident from the appearance of the two strong absorption bands at 290 and 365 mμ.[14] Thus if any triiodide ion is formed, a significant error can be introduced from the effective decrease of the iodine concentration along with the superposition of the 365-mμ triiodide absorption band with a high molar absorptivity on the respective cyclopolymethylenetetrazole–iodine complex absorption band at about 430 ± 5 mμ. In order to eliminate the interference from the residual azide, crude cyclopolymethylenetetrazole was treated with potassium permanganate in an acid media prior to the final purification by recrystallization. After this treatment no evidence for the triiodide ion was found in the spectra of the respective complexes not even when the concentrations of cyclopolymethylenetetrazole were four times greater than those used to obtain the needed data. The solvent, 1,2-dichloroethane, was selected because all of the cyclopolymethylenetetrazoles were soluble in it at concentrations greater than 1 *M*, and its vapor pressure at 35° was sufficiently low to allow convenient handling. In 1,2-dichloroethane, molecular iodine has an absorbance maximum at 495 mμ. The cyclopolymethylenetetrazoles essentially do not absorb in this spectral region. In all cases the concentrations of tetrazoles were kept below 0.6 *M*. With increasing tetrazole/I_2 ratio the absorption maximum gradually shifted from 495 to 430 ± 5 mμ. There was a slight shifting of the isosbestic point which can be attributed to the changing character of the solvent as the concentration of the cyclopolymethylenetetrazole was increased. A typical set of spectral curves is illustrated in Figure 3.

The respective formation constants were determined by using the spectrophotometric data taken at each of four temperatures for the cyclopolymethylenetetrazole solutions in 1,2-dichloroethane. These data were interpreted using a regression analysis of the data performed, as previously described[15] on a CDC 3600 computer.

The formation constants at the various temperatures obtained in this study are given in Table III. Further, by the use of the data given in Table III, a plot of the relationship between log K_f's and the reciprocals of the absolute temperatures was obtained by drawing a straight line to fit all the points as closely as possible by the least-squares method (Figure 4). The standard enthalpy, which was assumed to be independent of temperature over the 30° temperature span studied, was obtained from the slope of the straight line. The entropy change was then calculated for each of the respective temperatures.

Results and Discussion

Results obtained in the spectrophotometric part of this investigation are shown in Table III. It is seen that the donor properties of the cyclopolymethylenetetrazoles are rather weak. The formation constant for the $C_5MT \cdot I_2$ complex was reported as 7.5 in a previous publication;[5] however, that work was done in carbon tetrachloride solutions.

It is seen that in *vis ā vis* halogens the donor properties of the tetrazole ring are of the same order of magnitude as those of an aromatic ring.[16] In our case, however, the tetrazole–iodine bonding does not involve π electrons. In fact, it has been recently shown that in the solid $C_5MT \cdot ICl$ complex the bonding occurs through one of the nitrogen atoms.[17] Moreover, it has been shown in a previous publication[7] that in general the tetrazole ring has only very limited ability to form π complexes. Under these conditions the inductive effect of the polymethylene ring would not be too significant. The formation constants seem to increase with increasing length of the hydrocarbon chain, with the exception of pentamethylenetetrazole which does not fit into the series. The difference is substantially greater than the experimental error. This irregularity may be due to difference in the solvation of C_5MT as compared with the other homologs, since this compound is, by far, the most soluble of the series,

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both in water and in nonaqueous solvents. Physicochemical properties of other cyclopolymethylenetetrazoles are practically unknown at this time and will have to be investigated more thoroughly before possible reasons for the discrepancy can be advanced.

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Pseudohalogens. XI. *In Situ* Addition of Nitrosyl Formate to Olefins[1,2]

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Abstract: Nitrosyl formate, the lowest homolog of the nitrosyl acylate series, has been prepared *in situ* from isoamyl nitrite and formic acid and added to a number of acyclic-, alicyclic-, and aryl-substituted unsaturated compounds to yield novel, reactive formoxynitroso compounds. Addition proceeds best with olefins activated electronically (styrene, α- and β-methylstyrene) or sterically (norbornene, cyclohexene) toward electrophilic addition and poorly or not at all with mono- or disubstituted olefins. Markovnikov addition products are obtained. When the nitroso group becomes attached to a tertiary carbon atom, as in the adducts of 2,3-dimethyl-2-butene and Δ^9-octalin, products are blue monomers; in all other cases the products are colorless dimers. Monomeric 2,3-dimethyl-2-formoxy-3-nitrosobutane has the typical esr spectrum of a monoradical. Addition of nitrosyl formate to norbornene yields the *exo-cis* adduct without rearrangement, presumably by a four-center reaction. Addition to cyclohexene proceeds by *trans* addition. Further reactions of some of the nitrosyl formate addition products are described. Preliminary results of the addition of nitrosyl acetate and benzoate to unsaturated compounds are also discussed.

Acyl nitrites were first reported by Francesconi and Cialdea,[4] who obtained them by reaction of nitrosyl chloride with silver salts of carboxylic acids, the reaction of choice today. Other preparations of acyl nitrites include the reactions of (a) silver nitrite with acid chlorides,[5] (b) perfluorocarboxylic anhydrides with dinitrogen trioxide[6] and nitrosyl chloride,[7] and (c) saturated aqueous solutions of sodium nitrite with acetic, monochloroacetic, and trichloroacetic acids.[8] The two reported literature attempts[4,8] to prepare nitrosyl formate ended in failure with an explosion resulting in one case.[4] The most complete study of the preparation of acyl nitrites is that of Pritzkow and Nitzer,[9] who used the silver salt route[4] to obtain 14 compounds for study of their homolytic decomposition.

In this paper we are reporting (a) the *in situ* preparation and consumption of nitrosyl formate in the presence of suitable olefins, (b) properties and reactions of the resulting formoxynitroso adducts, (c) preliminary results of nitrosyl acetate and benzoate additions to unsaturated compounds, and (d) tentative conclusions concerning the stereochemistry and mechanism of some of the addition reactions.

Experimental Section

Equipment. Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137. Ultraviolet and visible spectra were taken on a Perkin-Elmer ultraviolet-visible recording spectrophotometer, Model 202. Nmr spectra were obtained with a Varian A-60A spectrometer using TMS as internal standard. Esr spectra were obtained with a Varian V 4500-10A, X-band spectrometer. Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Melting points and boiling points are uncorrected. Glpc separations were carried out with a Wilkens Aerograph Model 350-B dual column gas chromatograph with a thermal conductivity detector and a manual collector. Columns used are indicated below; helium was the carrier gas in all cases. Molecular weights were obtained on a Mechrolab Inc. vapor pressure osmometer, Model 301A. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del.

Materials. Formic acid (97%) was dried and then distilled from boric anhydride. It was stored over boric anhydride and filtered just before use. Unsaturated compounds were at least 98% pure (glpc): cyclohexene, 2,3-dimethyl-2-butene, 2-methyl-2-butene (Phillips Petroleum Co.); norbornene, norbornadiene, *trans*-propenylbenzene (Aldrich Chemical Co.); styrene, α-methylstyrene (Dow Chemical Co.); 1-hexadecene (Humphrey Chemical Co.); *trans*-3-hexene (Columbia Organic Chemicals Co.); and Δ^9-octalin.[10] Isoamyl nitrite was prepared as required.[11] Nitrosyl chloride was condensed from a cylinder; it was redistilled just before use. Nitrosyl tetrafluoroborate (K & K laboratories) and lithium aluminum hydride (Metal Hydrides, Inc.) were used as received. Solvents and reagents were the best quality; they were used without further purification.

***trans*-1-Formoxy-2-nitrosocyclohexane Dimer (1).** To formic acid (100 ml) cooled to 5° in a 500-ml, three-necked flask fitted with

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