The evidence we present in this paper indicates that this pattern will be followed in group VI heterocycles.

Summary

The barrier-to-ring reversal decreases monotonically on going down the column for group VI pentamethylene heterocycles, despite the fact the ring is becoinmg increasingly puckered. The lower barrier is associated with the smaller C–X torsional barrier, and angle-bending strain must be unimportant. The same pattern is observed for the oxides and dioxides of thiane and selenane (SO > SeO; $SO_2 > SeO_2$). For the selenium series, the prediction can be made that the order of torsional barriers should be dimethyl selenide ~ dimethyl selenoxide > dimethyl selenone, whereas in the sulfur series the predicted order is dimethyl sulfone ~ dimethyl sulfoxide (known) > dimethyl sulfide (known). Selenane 1-oxide is found to have a larger proportion of axial isomer (84%) than thiane 1-oxide (62%) because the longer carbon-selenium bond length produces more attractive 1,3 and 1,5 interactions. For the same reason, *Se*-methylselenanium iodide appears to be almost entirely axial, whereas *S*-methylthianium iodide is almost entirely equatorial, on the basis of the magnitude of the α-proton geminal coupling constant.

Experimental Section

Melting points were measured with a Hershberg apparatus and are uncorrected. Routine nmr spectra were recorded on Varian A-60 and T-60 spectrometers. Variable-temperature experiments were conducted on the 90-MHz Bruker HFX-10 spectrometer, equipped with a Nicolet 1074 signal-averaging computer. Temperatures were calibrated with a Wilmad low-temperature thermometer and are considered accurate to ±1°. Complete line-shape analyses were carried out on a CDC-6400 computer with a CalComp 565 plotter. Elemental analyses were performed by Miss H. Beck, Analytical Services Laboratory, Department of Chemistry, Northwestern University, and by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Selenane-*3,3,5,5-d*$_4$ (2). The method is an adaptation of that of McCullough and Lefohn[21] and has been described previously.[11a]

Selenane-*3,3,5,5-d*$_4$ 1-Oxide (4). A mixture of 0.75 g (0.005 mol) of deuterated selenane and 0.60 g (0.005 mol) of 30% H_2O_2 was shaken in a sealed tube until only one layer was present. After standing overnight, the solution was extracted three times with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. Removal of the drying agent and the solvent produced the crystalline but hygroscopic selenoxide. Recrystallization from benzene under anhydrous conditions gave 0.20 g of white crystals: mp 129–130.5° (sealed tube); nmr (CH_2Cl_2) δ 2.60 (br s, 4, α CH_2) and 1.50 (AB q, 2, J = 13.6 Hz, γ CH_2). *Anal.* Calcd for $C_5H_{10}OSe$: C, 36.36; H, 6.06. Found: C, 36.23; H, 6.10.

Selenane-*3,3,5,5-d*$_4$ 1,1-dioxide (5) was obtained by the same method as the selenoxide, with 2 equiv of H_2O_2 and some heating on a steam bath: mp 190–191°; nmr (CH_2Cl_2) δ 3.18 (s, 4, α CH_2) and 1.60 (s, 2, γ CH_2). *Anal.* Calcd for $C_5H_{10}O_2Se$: C, 33.15; H, 5.52. Found: C, 32.81; H, 5.63.

***Se*-Methylselenanium-*3,3,5,5-d*$_4$ iodide (*Se*-methylpentamethyleneselenonium iodide) (6)** was prepared by stirring the deuterated selenane (2) with an excess of CH_3I until a white precipitate had formed. The solid was filtered, washed with CH_2Cl_2, and dried to give a quantitative yield of the salt: mp 176–178° (sealed tube, sublimed); nmr (SO_2/CH_2Cl_2) δ 3.24 (AB q, 4, J = 12.4 Hz, α CH_2), 2.66 (s, 3, CH_3), and 1.65 (s, 2, γ CH_2). *Anal.* Calcd for $C_6H_{13}SeI$: C, 24.74; H, 4.47. Found: C, 24.43; H, 4.46.

***S*-Methylthianium-*3,3,5,5-d*$_4$ iodide (*S*-methylpentamethylenesulfonium iodide)** was prepared from thiane[12c] in the same manner as the selenium analog:[22] mp 196–197° (sealed tube, sublimed); nmr (SO_2/CH_2Cl_2) δ 3.24 (AB q, 4, J = 12.3 Hz, α CH_2), 2.66 (s, 2, γ CH_2), 1.98 (s, 3, CH_3). *Anal.* Calcd for $C_6H_{13}SI$: C, 29.51; H, 5.33. Found: C, 29.68; H, 5.48.

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[21] J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

[22] This material was first prepared by R. G. Keske, to whom we are grateful for the instructions.

Conformational and Stereochemical Consequences of Uniparticulate Electrophilic Additions to *cis*-Bicyclo[6.1.0]nonatrienes. Reactions with Tetracyanoethylene

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Abstract: Reaction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene and its *anti*-9-methyl and *anti*-9-chloro derivatives with TCNE produces bicyclic tetracyanocyclobutanes in which the four-membered moiety is trans fused to a cyclononatriene ring. The methyl and chlorine substituents have been found to occupy uniquely the 6 position and to be oriented stereochemically trans to H_1 and cis to H_9. These studies reveal that TCNE is functioning as a uniparticulate electrophile and suggest that intermediate dipolar species possessing the gross structural features of *trans*-1,3-bishomotropylium ions are transiently produced. In addition, the lack of reactivity of bicyclo[6.1.0]-nonatrienes endowed with syn-9 substituents attests to the involvement of the more strained folded conformation of the bicyclic triene. The causative factors underlying the greater reactivity of the less stable conformers and the kinetic preference of the electrophile for exo bonding at C_3 are discussed.

A number of mechanistically informative and synthetically useful applications of uniparticulate electrophilic addition have recently been reported and discussed.[4,5] The unusually effective capability of such reagents to intercept transient cationic interme-

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[1] Studies at The Ohio State University were supported in part by the National Science Foundation.

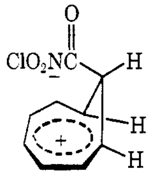
[2] Holder of a NATO Postdoctoral Fellowship, 1970–1972, administered by the Science Research Council.

[3] Financial support for the work at Iowa State University was provided by the U. S. Atomic Energy Commission.

[4] L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **93**, 4503 (1971), and pertinent references cited therein.

[5] D. J. Pasto, A. F. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).

diates which could otherwise pass undetected is of particular significance. Zwitterionic intermediates **1** and **2** represent certain of the species which have been generated (albeit not characterized) by this method and illustrate the promise of the technique for elucidation of reaction mechanism. The aim of the present study was to apply the mechanistically responsive characteristics of uniparticulate electrophilic processes to an examination of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**3**) reactivity in an effort to unravel the intricately interwoven dependence of conformation and stereochemistry in this polyolefinic system (*vide infra*).[6,7]



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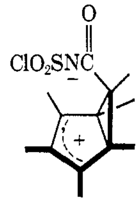

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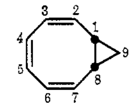
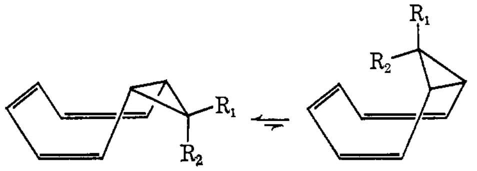


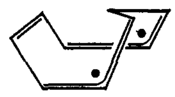
3

The parent hydrocarbon (**3**) appears to be a conformationally mobile structure capable of interconversion between the rather unconstrained extended tub conformation **4a** and the less stable folded arrangement **4b**. Interconversion of these conformers is seen to interchange in a very fundamental manner the spatial relationship of the C_9 substituents to the nonplanar triene moiety. *E.g.*, whereas R_2 is trans disposed relative to the most remote double bond in **4a**, it is positioned proximally to that olefinic linkage in **4b**. Additionally, transposition of **4a** into **4b** alters in an important way the alignment of $p\pi$ and internal cyclopropane orbitals such that the geometry adopted by the less stable conformer (**4b**) is more conducive to overlap.



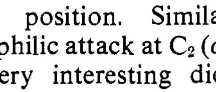
4a **4b**

To this date, the chief interest in **3** and its congeners derives from the variety of thermal isomerizations observed for these compounds.[8] Although the pathways proposed for these bond reorganizations remain controversial and the subject of ongoing study, the suggestion has been advanced by at least one group that an "orthogonal biradical" such as **5**, resulting from C_1–C_8 bond cleavage in the electronically more favorable but energetically less stable conformer (**4b**), may be involved at least in certain cases.[8a,9] Recent electrochemical studies of **3** support the contention; however, the conformer **4a** dominates the equilibrium in solution at room temperature.[10] Furthermore, the ability of a derivative of **3** to exist in conformer **4b** must necessarily be strongly influenced by the effective size of substituent R_2. When R_2 = H, relatively minor interaction of this substituent with the C_4–C_5 bond occurs; however, when R_2 = CH_3 or larger, severe nonbonded interactions are engendered, making conformer **4b** relatively unattainable for steric reasons. These same considerations can be expected to control the chemical reactivity of *cis*-bicyclo[6.1.0]nonatrienes under conditions of electrophilic addition.



5

A critical aspect of the electrophilic process involves appropriate assessment of the relationship between conformation and potential carbonium ion stabilization in **4a** and **4b**. Although the two conformers are capable of electrophilic attack at five possible sites, relative nucleophilicities dictate that bonding to an sp^2-hybridized carbon atom be kinetically preferred. As a direct result of the assumed tub conformations, however, there can be little conjugation through the triene systems since the $p\pi$ orbitals of adjacent double bonds are virtually orthogonal. Accordingly, attack at C_4 in either **4a** or **4b** will give rise to cations in which the respective vacant p orbitals are oriented spatially such that they are isolated geometrically from the neighboring vinyl group (*cf.* **6**). Thus, these positively charged entities will experience substantial destabilization by means of inductive electron withdrawal,[11,12] and the transition states leading to such carbonium ions are not expected to be attainable on a kinetically competitive basis (rate decelerations of as much as 10^3–10^4 are anticipated[11,12]). Needless to say, the cyclopropane ring also cannot come to the assistance of the cationic center because of its remote and relatively insulated position. Similar considerations apply to electrophilic attack at C_2 (*cf.* **7**).



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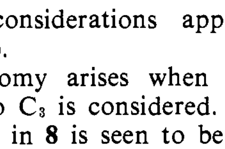

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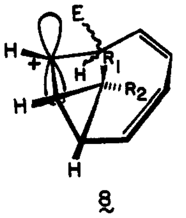

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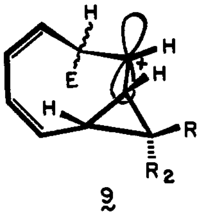

9

A very interesting dichotomy arises when initial bonding of an electrophile to C_3 is considered. Specifically, the vacant p orbital in **8** is seen to be more perfectly aligned for maximum overlap with the internal cyclopropyl bond such that attendant stabilization of the cationic center through delocalization will surely be operative. Conversely, the same orbital in **9** bisects

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(6) For a preliminary account of this research, see J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *J. Amer. Chem. Soc.*, **94**, 2904 (1972).

(7) The behavior of **3** toward chlorosulfonyl isocyanate is detailed in the accompanying paper: L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **95**, 4647 (1973).

(8) (a) A recent summary of the field has been made by S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971); (b) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **94**, 5845 (1972).

(9) However, see also A. G. Anastassiou and R. C. Griffith, *J. Chem. Soc. D*, 1301 (1971); 399 (1972).

(10) L. B. Anderson, M. J. Broadhurst, and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 2198 (1973).

(11) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); **92**, 1660 (1970).

(12) P. v. R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

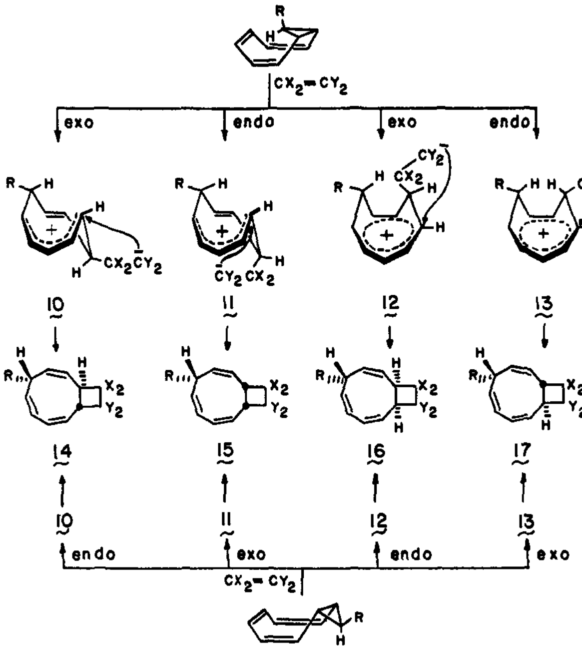
the three-membered ring;[13] as a consequence, pronounced destabilization of the cationic center will again be encountered in this instance.[11,12] These considerations mean that, under reasonable conditions, electrophilic additions to bicyclo[6.1.0]nonatrienes should occur at C_3 *via* conformer **4b** since it uniquely serves as the precursor to **8**. As already discussed, however, the ability of a derivative of **3** to exist in conformer **4b** is strongly influenced by the size of substituent R_2. On this basis, it was considered that bicyclo[6.1.0]nonatriene (**3**) and anti-9-substituted derivatives of this ring system should be quite susceptible to electrophilic reactions, whereas the corresponding syn-9-substituted isomers should react only slowly, if at all, in the midst of discriminating electrophiles.

Addition as depicted in **8** can lead with a small readjustment of bond angles to potentially delocalized 1,3-bishomotropylium cations.[14-16] Two additional questions now warrant consideration. (a) Will the methylene bridges in these carbocations be positioned cis (*e.g.*, **12** and **13**) or trans (*e.g.*, **10** and **11**) to one another? (b) Will the approaching electrophilic reagent exhibit preferential exo or endo bonding to **4b**? Both questions, as well as the preceding hypothesis concerning the necessary intervention of conformer **4b**, appeared resolvable by means of relatively few experiments involving suitable uniparticulate electrophiles.

Scheme I illustrates the fact that the formation of a trans- or cis-fused adduct is indirectly relatable to the stereochemistry of the bishomotropylium ion and the direction from which the uniparticulate electrophile (generalized here as $X_2C{=}CY_2$) has approached the triene. By making recourse to an anti-9-substituted derivative of **3**, the possibilities are narrowed still further. Now, the stereochemistry of a given product from among the set **14–17** becomes diagnostic not only of the gross structure of the cationic intermediate, but also of the stereochemical option exercised by the electrophile.

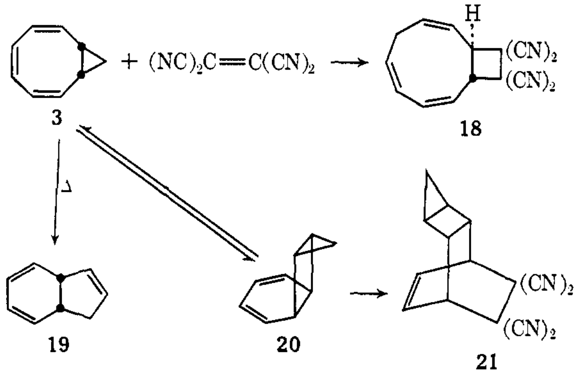
The four identical cycloadducts could also be produced from conformer **4a** (Scheme I). However, should the syn-9-substituted derivatives of **3** prove unreactive, complete analysis of the factors underlying the reactivity of **3** under electrophilic conditions would be made manifest.[17] The present study and the ensuing report[7] provide suggestions of the feasibility of such an extrapolation of the principles of conformation analysis to carbonium ion reactivity.

Scheme I



The recognized ionic character of TCNE additions to a large number of alkenes,[18] strained unsaturated hydrocarbons,[19] and cyclic polyolefins[20] suggested that the electronic delocalization potentially available in reaction with **3** might constitute a significant driving force for an ionic process. In actuality, the reaction of **3** with tetracyanoethylene had previously been shown to lead under appropriate conditions[21,22] to **18**, but detailed knowledge of the ring juncture stereochemistry was not available.

At the outset of the present investigation, conditions were sought which would preclude competitive, irreversible conversion of **3** to *cis*-8,9-dihydroindene (**19**), a process known to occur readily at 90°,[23] and reversible disrotatory cyclization to **20**. From available data,[21,23,24] it appeared that the concentration levels of



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[13] These conclusions were arrived at after consideration of a variety of molecular models in which the proton at C_2 was maintained in a near perfectly staggered orientation relative to the substituents (E and H) at C_3.

[14] It has previously been demonstrated by P. Warner and S. Winstein [*J. Amer. Chem. Soc.*, **93**, 1284 (1971)] that the protonation of *cis*-bicyclo[6.1.0]nona-2,4,6-triene in a 1:4 (v/v) mixture of FSO_3H–SO_2ClF at *ca.* −125° does result in the formation of a monocyclic 1,3-bishomotropylium ion.

[15] For a more recent study of such protonation, see L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *ibid.*, **95**, 3386 (1973).

[16] For simplicity and convenience at this point of the discussion, the *cis*- and *trans*-1,3-bishomotropylium cations of Scheme I are not represented equally as fully delocalized structures. In the ensuing discussion and particularly in the companion paper, this topic is given more detailed attention.

[17] The syn positioning of a group at C_9 results in endo placement of the R group in **10–13**, an outcome which is almost certainly energetically and sterically unrewarding. More important, however, is the realization that the orbital alignment in **4a** is not conducive to rupture of the cyclopropane ring at the height of the rate-determining transition state.

[18] P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

[19] See, for example: (a) S. Nishida, I. Moritani, and T. Teraji, *J. Chem. Soc. D*, 36 (1971); (b) J. E. Baldwin and R. E. Peavy, *J. Org. Chem.*, **36**, 1441 (1971); (c) J. E. Baldwin and R. K. Pinschmidt, Jr., *Tetrahedron Lett.*, 935 (1971); (d) R. Noyori, N. Hayashi, and M. Kato, *J. Amer. Chem. Soc.*, **93**, 4948 (1971).

[20] H.-P. Löffler, T. Martini, H. Musso, and G. Schröder, *Chem. Ber.*, **103**, 2109 (1970).

[21] W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970).

[22] C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970); *Tetrahedron*, **27**, 3285 (1971).

[23] E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961).

[24] J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Chem. Soc. D*, 820 (1971).

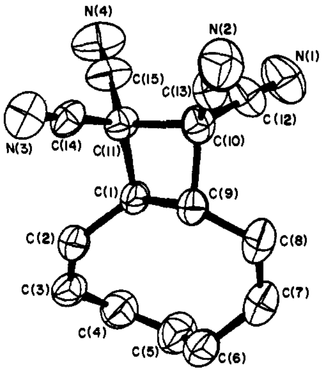


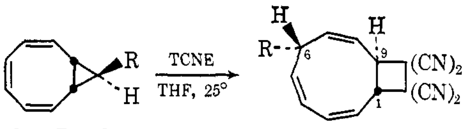
Figure 1. A structural view of **18** as determined by X-ray analysis showing the conformation of the molecule.

20 become such above 60° that divertive consumption of the potential electrophile *via* concerted ($_\pi 4 + _\pi 2$) cycloaddition (*cf.*, for example, **21**) competes exceedingly well with the desired stepwise process. Accordingly, recourse was made to the execution of all TCNE reactions in anhydrous tetrahydrofuran at room temperature under a nitrogen atmosphere.

When an equimolar mixture of **3** and TCNE was allowed to react in this fashion for 3.5 days, adduct **18** was isolated in 63.5% yield. The identity of **18** to previously isolated material[21,22,25] was apparent from its melting point, the electronic spectrum, and the temperature- and solvent-dependent nmr features. In particular, the protons at the ring juncture constitute an AB pattern with $|J_{AB}|$ = 10.7 Hz. The magnitude of this coupling constant was not considered necessarily diagnostic of the molecular stereochemistry for two reasons: (a) molecular models suggested that the nine-membered ring from either possible isomer could adopt a variety of conformations each of which engendered different degrees of twist in the cyclobutane ring with appreciable attendant changes in the relevant dihedral angle; (b) the coupling constants between syn and anti protons in 1,1,2,2-tetracyanocyclobutanes customarily exhibit appreciable variability.[26] Ultimately, the three-dimensional features of **18** were established by X-ray diffraction analysis.

The final three-dimensional structure of **18** (Figure 1) reveals clearly that the hydrogens common to the two rings are trans disposed and that the puckering of the cyclobutane ring is a relatively standard 21°. The bond distances in the four-membered ring vary from 1.57 to 1.59 Å. The torsional angle about the double bonds are all less than 3° while the torsional angle about the single bond of the butadiene moiety is 57°. In general, all bond distances and angles agree well with accepted values.

When equimolar quantities of **22a** and TCNE were allowed to react under the predescribed conditions for 3.5 days, a single adduct (**23a**) was produced in 69% yield. The assignment of structure to **23a** is based chiefly on spectral considerations. Thus, the lone ultraviolet maximum (ethanol solution) at 231 nm (ϵ 11,240) in reconcilable with the fact that the added methyl group at C_6 produces a higher level of planarity in the conjugated diene moiety relative to **18**

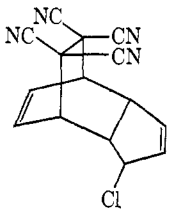


22a, R = CH$_3$
b, R = Cl

23a, R = CH$_3$
b, R = Cl

[$\lambda_{max}^{C_2H_5OH}$ 225 nm (ϵ 7250)] quite likely because of steric factors. The nmr spectrum shows the presence of six olefinic protons (m at δ 5.1–6.5), two ring juncture hydrogens (AB pattern with small additional couplings, $|J_{AB}|$ = 11 Hz, at 4.45 and 4.00), a doubly allylic proton (m at 3.4), and the methyl group (d, J = 7 Hz, at 1.13). Unfortunately, this adduct did not afford crystals suitable for X-ray diffraction study. The trans nature of the ring juncture and the stereochemistry at C_6 are, however, supported by the marked spectral similarities of **23a** to **23b** (see below) and by the established behavior of **22a** toward chlorosulfonyl isocyanate under comparable conditions.[7,27]

The more labile *anti*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene (**22b**) was next examined.[28] The propensity of **22b** for skeletal rearrangement has been amply demonstrated under conditions of neat thermal isomerization[29,30] and supported further by the report that reaction with TCNE in tetrahydrofuran at room temperature affords **24** in 50% yield.[29,31] In our hands, treatment of **22b** with TCNE in the customary fashion led chiefly to **24**. However, careful processing of the mother liquors lent itself to the isolation of **23b**. The ultraviolet spectrum of this adduct in ethanol reveals a maximum at 226 nm (ϵ 11,110). The nmr spectrum (60 MHz, CDCl$_3$) shows resonance signals at δ 5.4–6.6 (m, 7, olefinic and doubly allylic protons) and 4.4 (AB pattern, $|J_{AB}|$ = 11 Hz, 2, ring juncture protons).



24

The structure and stereochemistry of **23b** were simultaneously revealed by three-dimensional X-ray crystal structure analysis. As can be seen in Figure 3, the ring fusion stereochemistry is again such that the relevant hydrogens are trans disposed. In addition, the chlorine atom occupies the 6 position and is oriented stereochemically such that it is trans to H$_1$ and cis to H$_9$. The conformational effect of the halogen substituent reduces the puckering angle of the cyclobutane ring to 19° and the torsional angle about the single bond of the butadiene segment to 47° (compare **18**).

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(25) T. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

(26) J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962).

(27) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972).

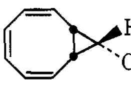
(28) As a result of difficulties inherent in the separation of pure **22b** from the syn counterpart, a sample of chlorocarbon enriched in the anti isomer (anti/syn = 23/5) was utilized herein.

(29) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

(30) J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *ibid.*, **93**, 279 (1971).

(31) The mechanism of conversion of **22b** to **24** is not known. The rate of formation of **24** is significantly faster than the rate of rearrangement of **22b** to dihydroindenyl chloride at room temperature. Conceivably, rearrangement within the TCNE charge-transfer complex is operative.

Meaningful, *syn*-9-methyl isomer **25** did not react with TCNE after 3.5 days (91% recovery). A similar lack of reactivity was observed with 9,9-dimethyl derivative **26** (91% recovery).



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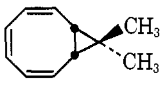

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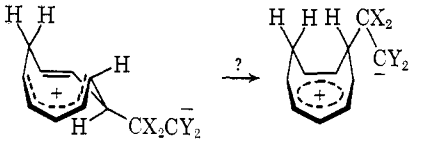
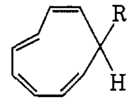
Establishment of the trans ring juncture of adducts **18** and **23** brings with it insight into the mechanism of this intriguing reaction. The stereochemical data, when taken in consort with the observations that only anti-9 and not syn-9 substituted *cis*-bicyclo[6.1.0]nonatrienes react with TCNE under the stated conditions, seemingly point to that pathway which involves initial electrophilic attack of TCNE at C_3 of the less stable bicyclononatriene folded conformation **4b**. Molecular models show that exo bonding of the electrophile to C_3 of **4b** and opening of the central bond first positions the two carbon bridges on opposite surfaces of the seven-membered cationic ring. In other words, *cis*-1,3-bishomotropylium ions (*e.g.*, **12** and **13**) are not the products of kinetically controlled electrophilic attack on **4b**. Rather, if cisoid cations are produced under certain conditions, they very probably arise from subsequent structural reorganization of first-formed trans isomers. Since methylene bridge inversion does occur in the homotropylium series,[32] it is obvious that such processes could operate in 1,3-bishomotropylium salts as well. However, inversion of the electrophile bearing bridge in **10**, if operative, is not of kinetic significance, for this process would give rise to zwitterion **12** which would ultimately furnish cis adduct of type **16** or a product of quite different structure[7] (not seen). No information is available on the conformational mobility of the second tetrahedral carbon. Inversion of that bridge after rate-determining formation of **10** cannot be ruled out, particularly when R = H. When R ≠ H, however, inversion of this center in **10** would position R in the more sterically crowded endo environment.



This maneuver is recognized[15] to be energetically unrewarding and, although possible, is not entirely likely. We emphasize that conformational interconversion of this bridge does not affect the stereochemical outcome of the reaction. The trans ring juncture requires only that collapse of the zwitterion with C–C bond formation occur with the electrophilic residue in an exo orientation. The configuration of the C_6 carbon atom becomes fixed at the time of exo attack by the TCNE at C_3 of the folded conformation of the bicyclo[6.1.0]nonatrienes.

To this point, we have assumed efficient electrophilic interception of folded *cis*-bicyclo[6.1.0]nonatriene conformers (*i.e.*, **4b**) by the TCNE. The alternate possibility of cycloaddition to cis^4-cyclononatetraenes (conceivably present in low concentration[8]) is not tenable in view of the fact that suitable control experiments proved negative.[22] Likewise, concerted $({}_{\pi}2 + {}_{\pi}8)$ cycloaddition to the *cis*-bicyclo[6.1.0]nonatrienes[21] is incompatible with the structural results. The stereochemical outcome is also irreconcilable with the operation of concerted $({}_{\pi}2_a + {}_{\pi}2_s)$ bonding to the trans olefinic center of cis^2,*trans*,*cis*-cyclononatetraenes (**27**), intermediates which have been proposed to arise transiently at more elevated temperatures.[33,34]



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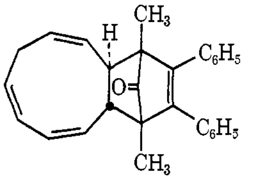
In contrast, the postulate of stepwise $({}_{\pi}2 + {}_{\pi}2)$ cycloaddition to **27** is possibly compatible with the high level of stereoselectivity associated with the substituent at C_6 in **23a** and **23b**. A suitable test of the inoperative nature of this latter pathway would appear to reside in the utilization of an unsymmetrical uniparticulate electrophile in tandem with alkyl substitution of the cyclic polyolefin. This aspect of the problem is addressed in the following paper. Suffice it to point out at this time that if **27** is involved, two isomeric products (and possibly as many as four when R ≠ H) should result unless directional specificity arising from differences in degree of possible charge delocalization commands major importance. However, when all of these conditions are met as in the case of chlorosulfonyl isocyanate, impressively stereocontrolled additions are consistently observed.[6,27,35]

In this light, the recent trapping experiments of Anastassiou and Griffith[33] warrant discussion. When **3** was heated at reflux with an equimolar quantity of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (DDCD) in benzene, three 1:1 adducts characterized as the product of reaction with *cis*-8,9-dihydroindene (25%), **28** (45%), and **29** (30%) were isolated. As noted by these researchers, the formation of **28** and **29** is most reasonably viewed as the result of thermally allowed $({}_{\pi}2_s + {}_{\pi}4_s)$ cycloaddition to **27** (R = H). The production of the two stereoisomeric adducts attests to the asymmetry inherent in **27** (R = H). In brief, the TCNE and DDCD reactions differ most ostensibly in two ways. Firstly, the temperature of refluxing benzene is sufficient to engender conversion of **3** to *cis*-8,9-dihydroindene and the opportunity for reaction with any of the potential intermediates in this transformation[8] presents itself. In THF at room temperature, **3** is stable for quite long periods of time and accordingly this potential complication is greatly minimized. Secondly, DDCD is a 4π reactant while TCNE is not. The highly favorable stereoelectronic and kinetic factors associated with Diels–Alder reactions, at least relative



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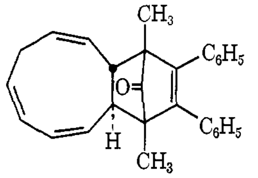

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Table I. Atom Positions and Thermal Parameters for **18**[a,b]

Atoms	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.5013 (2)	−0.1012 (4)	0.3483 (1)	0.0037 (1)	0.0214 (7)	0.0011 (1)	−0.0000 (3)	0.0001 (1)	0.0004 (1)
C(2)	0.4720 (2)	0.0778 (5)	0.3200 (1)	0.0045 (2)	0.0218 (8)	0.0011 (1)	0.0001 (3)	0.0003 (1)	0.0006 (2)
C(3)	0.3898 (2)	0.1169 (5)	0.3078 (1)	0.0050 (2)	0.0267 (9)	0.0012 (1)	0.0017 (3)	0.0001 (1)	0.0001 (2)
C(4)	0.3136 (2)	0.0079 (6)	0.3251 (1)	0.0046 (2)	0.0334 (10)	0.0018 (1)	0.0012 (4)	−0.0002 (1)	−0.0002 (2)
C(5)	0.2935 (2)	−0.0248 (6)	0.3758 (1)	0.0046 (2)	0.0353 (11)	0.0021 (1)	−0.0004 (4)	0.0003 (1)	0.0005 (2)
C(6)	0.3418 (2)	0.0515 (6)	0.4235 (1)	0.0056 (2)	0.0315 (10)	0.0015 (1)	0.0021 (4)	0.0006 (1)	0.0001 (2)
C(7)	0.3819 (2)	−0.1085 (6)	0.4560 (1)	0.0057 (2)	0.0332 (10)	0.0014 (1)	−0.0016 (4)	0.0008 (1)	0.0006 (2)
C(8)	0.4618 (2)	−0.1732 (5)	0.4499 (1)	0.0059 (2)	0.0247 (9)	0.0012 (1)	−0.0011 (4)	0.0005 (1)	0.0009 (2)
C(9)	0.5258 (2)	−0.1019 (4)	0.4093 (1)	0.0045 (1)	0.0196 (7)	0.0011 (1)	0.0002 (3)	0.0000 (1)	0.0003 (2)
C(10)	0.6017 (2)	−0.2458 (4)	0.3958 (1)	0.0042 (1)	0.0182 (6)	0.0013 (1)	−0.0003 (3)	−0.0002 (1)	0.0001 (1)
C(11)	0.5966 (2)	−0.1709 (4)	0.3356 (1)	0.0037 (1)	0.0218 (7)	0.0011 (1)	0.0000 (3)	−0.0001 (1)	−0.0007 (1)
C(12)	0.5752 (2)	−0.4485 (4)	0.4005 (1)	0.0055 (2)	0.0194 (8)	0.0018 (1)	0.0005 (3)	−0.0007 (1)	0.0003 (2)
C(13)	0.6837 (2)	−0.2111 (5)	0.4246 (1)	0.0049 (2)	0.0214 (8)	0.0013 (1)	0.0001 (3)	−0.0002 (1)	0.0007 (2)
C(14)	0.6578 (2)	−0.0118 (5)	0.3278 (1)	0.0038 (1)	0.0259 (8)	0.0259 (1)	0.0012 (3)	0.0002 (1)	−0.0003 (2)
C(15)	0.6043 (2)	−0.3150 (5)	0.2925 (1)	0.0037 (1)	0.0274 (9)	0.0018 (1)	0.0008 (3)	−0.0004 (1)	−0.0019 (2)
N(1)	0.5531 (3)	−0.6036 (5)	0.4054 (2)	0.0089 (2)	0.0215 (7)	0.0030 (1)	−0.0013 (3)	−0.0008 (1)	0.0005 (2)
N(2)	0.7447 (2)	−0.1756 (5)	0.4480 (1)	0.0054 (2)	0.0358 (10)	0.0018 (1)	−0.0004 (3)	−0.0008 (1)	0.0006 (1.9)
N(3)	0.7052 (2)	0.1135 (5)	0.3241 (1)	0.0056 (2)	0.0330 (9)	0.0019 (1)	−0.0022 (3)	0.0004 (1)	0.0000 (2)
N(4)	0.6055 (2)	−0.4227 (5)	0.2588 (1)	0.0064 (2)	0.0407 (10)	0.0025 (1)	0.0018 (4)	−0.0004 (1)	−0.0054 (2)
H(1)	0.4435	−0.1775	0.3361						
H(2)	0.5208	0.1817	0.3087						
H(3)	0.3784	0.2412	0.2829						
H(4)	0.2711	−0.0488	0.2946						
H(5)	0.2377	−0.1145	0.3835						
H(6)	0.2971	0.1302	0.4487						
H(7)	0.3426	−0.1750	0.4866						
H(8)	0.4828	−0.2866	0.4764						
H(9)	0.5358	0.0344	0.4293						
H(10)	0.3924	0.1472	0.4099						

[a] Estimated standard deviations (shown in parentheses) are right justified to the least significant digit of the preceding number. [b] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. The hydrogen atoms were given an isotropic temperature factor of 6 Å^2 which was not varied.

to thermal ($_\pi2 + {}_\pi2$) cycloadditions, will undoubtedly favor processes such as those which result in the formation of **28** and **29**. In a sense this is fortunate, for this phenomenon is probably the major contributing factor to the ability of TCNE to function as a unparticulate electrophile.

Experimental Section

Reaction of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene with TCNE. To a solution of TCNE (1.28 g, 0.01 mol) in dry tetrahydrofuran (7 ml) under a nitrogen atmosphere was added 1.18 g (0.01 mol) of **3** ($R_1 = R_2 = H$). A deep amber color developed immediately. The reaction mixture was allowed to stand at ambient temperature for 3.5 days and solvent was then evaporated to yield a brown oil which crystallized on trituration with a little ether–pentane (1:1). This product was dissolved in dichloromethane and rapidly filtered through a Florisil column (1 × 10 cm) to remove a small amount of unreacted TCNE. After evaporation of the solvent, colorless crystals (1.56 g, 63.5%) were obtained. Recrystallization from carbon tetrachloride gave **18** as long colorless needles, mp 141–141.5° (lit.[21,22] mp 140.5–141°; mp 141–141.5°).

Clear acicular crystals of **18** were obtained by slow evaporation of a methylene chloride solution. Preliminary X-ray photographs revealed Laue symmetry of *mmm* which placed the crystal in the orthorhombic space system. Systematic extinctions were observed for $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h + k = 2n + 1$) and uniquely determined the space group to be *Pbcn* (D_{2h}^{14}). A congruent calculated and experimental density (ρ = 1.23 g/cm^3) disclosed $Z = 8$ (or one molecule per asymmetric unit). A crystal with approximate dimensions of 0.15 × 0.10 × 0.10 mm was mounted with b coincident with the ϕ axis of the fully-automated Hilger–Watts four-circle diffractometer equipped with a scintillation detector system. From accurately measured θ values, cell constants were calculated to be a = 15.41 (1) Å, b = 6.93 (1) Å, c = 24.97 (1) Å. Data were collected at room temperature for the hkl octant within a 2θ sphere of 50° using Zr-filtered Mo Kα radiation (0.7107 Å). An ω–2θ scan technique was employed with backgrounds measured at $\theta_{hkl} \pm (0.25 + 0.01 \times \theta_{hkl})$. Throughout data collection, periodic measurements were made on three assigned standard reflections to assess crystal and electronic stability. The intensities were corrected for Lorentz and polarization factors and the estimated deviation of the intensity, $\sigma(I)$, was based on [(total count) + (background count) + 5% (total count)^2 + 5% (background count)^2]$^{1/2}$. The estimated deviation of F, $\sigma(F)$, was calculated from $\sigma(F) = \{[I + \sigma(I)]/L_P\}^{1/2}$.[36] A total of 2220 reflections were judged observed using the criterion that $F \geq 3\sigma(F)$ for any data to be observed. Corrections were not made for anomalous dispersion, absorption (μ = 0.835 cm^{-1}), or decomposition.

Solution and Refinement. Normalized structure factors were calculated in a standard way from a Wilson plot.[37] Phases were assigned to 436 E's greater than 1.5 by the iterative application of Sayre's equation.[38] An E map was computed from the most consistent set of phased E's, and all 20 nonhydrogen atom positions were located.[39] Full-matrix least-squares refinements on $\Sigma w \| F_o| - |F_c \|^2$, where $w = (1/\sigma[F])^2$, with anisotropic temperature factors reduced the conventional weighted and unweighted discrepancy index to R = 13.6% and wR = 11.0%. At this point, hydrogen positions were calculated for the trigonal and tetrahedral carbon atoms with bond distances set at 1.08 Å. Introducing the hydrogens and refining the parameters of the nonhydrogen atoms (321 parameters) lowered the weighted discrepancy index to wR = 9.4% and the unweighted to R = 8.5%. The scattering factor tables used were those of Hanson, *et al.*[40] In Table I are listed the final X-ray coordinates and the thermal parameters, respectively, along with their standard deviations.[41] The final bond distances and bond angles along with their standard deviations are listed in

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Table II. Selected Bond Distances in **18**[a,b]

Atoms	Distances, Å	Atoms	Distances, Å
C(1)-C(2)	1.498 (4)	C(9)-C(10)	1.573 (4)
C(1)-C(9)	1.568 (4)	C(10)-C(11)	1.591 (4)
C(1)-C(11)	1.580 (4)	C(10)-C(12)	1.467 (4)
C(2)-C(3)	1.332 (4)	C(10)-C(13)	1.474 (4)
C(3)-C(4)	1.462 (5)	C(11)-C(14)	1.465 (4)
C(4)-C(5)	1.324 (5)	C(11)-C(15)	1.473 (4)
C(5)-C(6)	1.502 (5)	C(12)-N(1)	1.134 (4)
C(6)-C(7)	1.508 (5)	C(13)-N(2)	1.135 (4)
C(7)-C(8)	1.319 (5)	C(14)-N(3)	1.139 (4)
C(8)-C(9)	1.500 (4)	C(15)-N(4)	1.125 (4)

[a] All carbon-hydrogen bond distances were set at 1.08 Å. [b] The estimated standard deviations are shown in parentheses.

Table III. Selected Bond Angles in **18**[a]

Atoms	Angle, deg	Atoms	Angle, deg
C(2)-C(1)-C(9)	122.2 (3)	C(9)-C(10)-C(12)	112.6 (3)
C(2)-C(1)-C(11)	116.0 (2)	C(9)-C(10)-C(13)	115.4 (2)
C(9)-C(1)-C(11)	88.2 (2)	C(11)-C(10)-C(13)	116.7 (2)
C(1)-C(2)-C(3)	124.3 (3)	C(12)-C(10)-C(13)	110.8 (3)
C(2)-C(3)-C(4)	126.4 (3)	C(1)-C(11)-C(10)	87.5 (2)
C(3)-C(4)-C(5)	123.9 (3)	C(1)-C(11)-C(14)	113.3 (2)
C(4)-C(5)-C(6)	125.7 (3)	C(1)-C(11)-C(14)	115.4 (2)
C(5)-C(6)-C(7)	111.8 (3)	C(10)-C(11)-C(14)	109.9 (2)
C(6)-C(7)-C(8)	124.9 (3)	C(10)-C(11)-C(15)	117.7 (3)
C(7)-C(8)-C(9)	125.5 (3)	C(14)-C(11)-C(15)	111.2 (2)
C(8)-C(9)-C(1)	119.9 (3)	N(1)-C(12)-C(10)	177.9 (3)
C(8)-C(9)-C(10)	115.2 (3)	N(2)-C(13)-C(10)	176.2 (4)
C(10)-C(9)-C(1)	88.5 (2)	N(3)-C(14)-C(11)	176.9 (3)
C(9)-C(10)-C(11)	87.7 (2)	N(4)-C(15)-C(11)	176.2 (3)

[a] The standard deviation is calculated from the inverse matrix of least-squares refinement.

Tables II and III.[42] Figures 1 and 2 show the final X-ray model for a single molecule and a unit cell respectively.[43] Table IV contains the observed and calculated structure factors.[44]

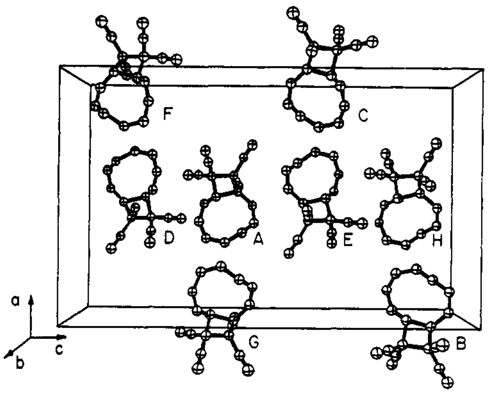

Figure 2. A computer generated drawing of the unit cell of **18**. A is the reference molecule at (x, y, z). The other molecules are generated in the following way: B ($^1/_2 - x$, $^1/_2 - y$, $^1/_2 + z$); C ($^1/_2 + x$, $^1/_2 - y$, $^1/_2 - z$); D ($1 - x$, y, $^1/_2 - z$); E ($1 - x$, $1 - y$, $1 - z$); F ($^1/_2 + x$, $^1/_2 + y$, $^1/_2 - z$); G ($^1/_2 - x$, $^1/_2 + y$, z); H (x, $-y$, $^1/_2 + z$).

Cycloadditon of 22a and TCNE. Treatment of 1.32 g (0.01 mol) of **22a**[45] with 1.28 g (0.01 mol) of TCNE in 7 ml of dry tetrahydrofuran as above (3.5 days) afforded 1.8 g (69%) of **23a** after chromatographic purification; colorless crystals, mp 152–153° (from dichloromethane–ether).

Reaction of 22b with TCNE. A solution of 3.04 g (0.02 mol) of **22b**[29] (anti/syn = 23/5) in dry tetrahydrofuran (10 ml) containing 2.6 g (0.02 mol) of TCNE was allowed to stand for 25° for 1 week. The crude pale brown solid obtained upon solvent evaporation was directly recrystallized from methylene chloride–ether to give 1.3 g (23%) of **24** as colorless crystals, mp 229–231° dec (lit.[29] mp 230–231° dec).

Evaporation of the combined mother liquors yielded a crystalline residue, mp 170–190°, nmr analysis of which clearly revealed that the substrate was a mixture of **23b** and **24**. Repeated recrystallizations of this material from ether eventually afforded a pure sample of **23b** as colorless crystals, mp 204–206° dec.

Table V. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for **23b**[a]

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.1936 (2)	−0.3429 (2)	0.8832 (1)	0.0311 (5)	0.0147 (3)	0.0065 (1)	−0.0053 (3)	−0.0061 (2)	0.0038 (1)
C(1)	0.5246 (7)	0.2735 (7)	0.7093 (3)	0.012 (1)	0.012 (1)	0.0036 (3)	0.0020 (8)	−0.0029 (4)	0.0012 (4)
C(2)	0.4181 (7)	0.0924 (7)	0.6732 (4)	0.016 (1)	0.016 (1)	0.0043 (3)	−0.0018 (9)	−0.0037 (5)	0.0004 (5)
C(3)	0.3262 (8)	−0.0690 (8)	0.7284 (4)	0.017 (1)	0.014 (1)	0.0049 (3)	−0.001 (1)	−0.0034 (5)	0.0008 (5)
C(4)	0.3117 (8)	−0.0929 (7)	0.8362 (4)	0.017 (1)	0.013 (1)	0.0050 (3)	−0.0007 (9)	−0.0015 (5)	0.0023 (5)
C(5)	0.2018 (9)	0.0417 (8)	0.8902 (4)	0.022 (1)	0.016 (1)	0.0049 (4)	0.003 (1)	−0.0011 (6)	0.0030 (5)
C(6)	0.2716 (9)	0.1419 (9)	0.9384 (4)	0.026 (2)	0.018 (1)	0.0041 (3)	0.002 (1)	−0.0011 (6)	0.0017 (6)
C(7)	0.4725 (9)	0.2496 (8)	0.9470 (4)	0.030 (2)	0.014 (1)	0.0039 (3)	−0.000 (1)	−0.0032 (6)	0.0005 (5)
C(8)	0.6322 (8)	0.2719 (8)	0.8813 (4)	0.022 (1)	0.016 (2)	0.0036 (3)	0.001 (1)	−0.0028 (6)	0.0016 (5)
C(9)	0.6728 (7)	0.2569 (7)	0.7710 (3)	0.012 (1)	0.014 (1)	0.0036 (3)	−0.0026 (8)	−0.0033 (4)	0.0024 (4)
C(10)	0.8088 (6)	0.4475 (7)	0.7103 (3)	0.0093 (9)	0.014 (1)	0.0035 (3)	0.0021 (8)	−0.0022 (4)	0.0010 (4)
C(11)	0.6930 (7)	0.4065 (7)	0.6283 (4)	0.012 (1)	0.014 (1)	0.0037 (3)	0.0000 (9)	−0.0029 (4)	0.0021 (5)
C(12)	0.6441 (7)	0.5769 (8)	0.5857 (4)	0.013 (1)	0.016 (1)	0.0037 (3)	0.0018 (9)	−0.0023 (4)	0.0012 (5)
C(13)	0.7878 (3)	0.2993 (8)	0.5506 (4)	0.016 (1)	0.015 (1)	0.0034 (3)	0.0018 (9)	−0.0020 (5)	0.0008 (5)
C(14)	1.0107 (1)	0.4342 (7)	0.6827 (4)	0.013 (1)	0.015 (1)	0.0048 (3)	0.0008 (9)	−0.0028 (5)	0.0008 (5)
C(15)	0.7854 (7)	0.6260 (8)	0.7561 (4)	0.013 (1)	0.018 (1)	0.0041 (3)	0.0009 (9)	−0.0020 (5)	0.0015 (5)
N(1)	0.6050 (8)	0.7020 (7)	0.5545 (4)	0.026 (1)	0.022 (1)	0.0056 (3)	0.009 (1)	−0.0038 (5)	0.0013 (5)
N(2)	0.8640 (8)	0.2224 (8)	0.4895 (4)	0.026 (1)	0.029 (2)	0.0050 (3)	0.008 (1)	−0.0026 (5)	−0.0015 (6)
N(3)	1.1645 (7)	0.4168 (8)	0.6652 (4)	0.017 (1)	0.025 (1)	0.0074 (4)	0.0057 (9)	−0.0050 (5)	−0.0005 (6)
N(4)	0.7622 (7)	0.7703 (8)	0.7924 (4)	0.025 (1)	0.019 (1)	0.0063 (3)	0.006 (1)	−0.0039 (5)	−0.0023 (5)

[a] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. The estimated standard deviation is given in parentheses for the least significant figure.

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(42) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(43) C. K. Johnson, "ORTEP, A Fortram Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(44) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4639. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(45) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969).

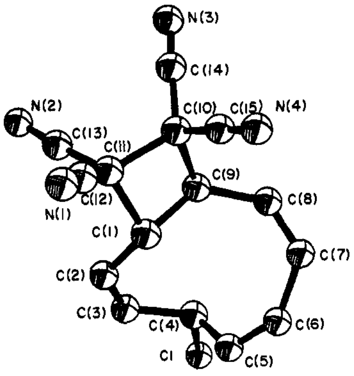

Figure 3. A structural view of **23b** as determined by X-ray analysis showing the conformation of the molecule.

Table VI. Selected Bond Lengths in **23b**[a]

Atoms	Distances, Å	
C(1)-C(2)		1.51 (1)
C(1)-C(9)	1.568 (6)	1.56 (1)
C(1)-C(11)	1.585 (7)	1.58 (1)
C(2)-C(3)	1.315 (7)	1.32 (1)
C(3)-C(4)	1.499 (8)	1.50 (1)
C(4)-Cl	1.813 (5)	1.81 (1)
C(4)-C(5)	1.472 (8)	1.47 (1)
C(5)-C(6)	1.343 (8)	1.34 (1)
C(6)-C(7)	1.489 (9)	1.50 (1)
C(7)-C(8)	1.292 (8)	1.31 (1)
C(8)-C(9)	1.521 (7)	1.52 (1)
C(9)-C(10)	1.580 (6)	1.58 (1)
C(10)-C(11)	1.589 (6)	1.58 (1)
C(10)-C(14)	1.470 (6)	1.47 (1)
C(10)-C(15)	1.438 (7)	1.44 (1)
C(11)-C(12)	1.464 (7)	1.46 (1)
C(11)-C(13)	1.461 (8)	1.46 (1)
C(12)-N(1)	1.133 (7)	1.13 (1)
C(13)-N(2)	1.122 (7)	1.12 (1)
C(14)-N(3)	1.134 (6)	1.13 (1)
C(15)-N(4)	1.164 (7)	1.16 (1)

[a] The estimated standard deviation is given in parentheses for the least significant figure.

Anal. Calcd for $C_{15}H_9ClN_4$: C, 64.16; H, 3.23; N, 19.97. Found: C, 64.26; H, 3.35; N, 20.01.

Crystals of **23b** were grown by slow evaporation of methylene chloride solutions. Microscopic examination revealed clear crystals with well-defined faces. A crystal with approximate dimensions of 0.15 × 0.10 × 0.10 mm was selected for diffraction work. Laue symmetry of $\bar{1}$ and the absence of any systematic extinctions defined the space group as either $P_{\bar{1}}(C_i^1)$ or $P_1(C_1^1)$. A calculated and observed density of 1.36 g/cm^3 for $Z = 2$ indicated one molecule per asymmetric unit for the presumed space group $P_{\bar{1}}$.

A crystal mounted on the *c* axis was transferred to a fully-automated Hilger–Watts four-circle diffractometer with a scintillation detector system. Cell constants of $a = 7.37(2)$ Å, $b = 6.97(3)$ Å, $c = 14.07(2)$ Å, $\alpha = 88.6(1)°$, $\beta = 76.3(1)°$, and $\gamma = 101.7(1)°$ were obtained from a least-squares fit of accurately measured θ values. All data within a 2θ sphere of 50° for the hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ octants were collected using Zr-filtered Mo Kα radiation (0.7107 Å). A moving crystal–moving counter scan technique was used with background measured at $\theta_{hkl} \pm (0.25 \times 0.01 \times \theta_{hkl})$. Periodic measurements of three assigned standard reflections were checked to appraise crystal and electronic stability. A decline of ~10% was noticed in the intensities of the standard reflections. No correction for this effect was made. The intensities were corrected for Lorentz and polarization factors, and $\sigma(I)$ was estimated from [(total count) + (background) + 5% (background)^2]$^{1/2}$. The estimated deviation of F, $\sigma(F)$, was calculated from $\sigma(F) = \{[I + \sigma(I)]/L_P\}^{1/2} - (I/L_P)^{1/2}$.[36] Of the 2332 reflections measured, 1736 were judged observed ($F < 3\sigma(F)$). A small calculated linear absorption coefficient of 2.1 cm^{-1} indicated that no absorption correction was necessary.

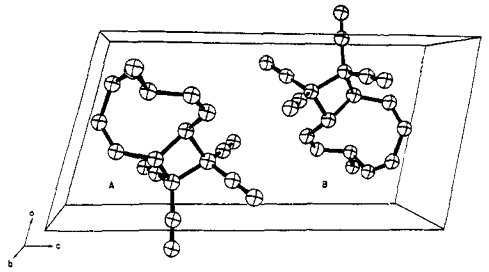

Figure 4. A computer generated perspective drawing of the unit cell of **23b**.

Table VII. Selected Bond Angles in **23b**

Atoms	Angles, deg	
C(2)-C(1)-C(9)		120 (1)
C(2)-C(1)-C(11)	115.1 (4)	115 (1)
C(9)-C(1)-C(11)	88.4 (3)	88 (1)
C(1)-C(2)-C(3)	124.8 (5)	124 (1)
C(2)-C(3)-C(4)	123.3 (5)	123 (1)
C(3)-C(4)-C(5)	111.1 (5)	111 (1)
C(3)-C(4)-Cl	109.8 (5)	110 (1)
Cl-C(4)-C(5)	108.6 (5)	109 (1)
C(4)-C(5)-C(6)	125.6 (6)	126 (1)
C(5)-C(6)-C(7)	125.9 (6)	126 (1)
C(6)-C(7)-C(8)	130.7 (5)	131 (1)
C(7)-C(8)-C(9)	130.9 (5)	131 (1)
C(8)-C(9)-C(10)	113.7 (5)	114 (1)
C(1)-C(9)-C(8)	123.5 (5)	123 (1)
C(1)-C(9)-C(10)	88.8 (3)	89 (1)
C(9)-C(10)-C(11)	87.8 (3)	88 (1)
C(9)-C(10)-C(14)	113.2 (5)	113 (1)
C(9)-C(10)-C(15)	113.5 (5)	113 (1)
C(11)-C(10)-C(14)	116.7 (4)	117 (1)
C(11)-C(10)-C(15)	112.3 (4)	112 (1)
C(14)-C(10)-C(15)	111.4 (5)	111 (1)
C(1)-C(11)-C(10)	87.9 (3)	88 (1)
C(1)-C(11)-C(12)	115.0 (4)	115 (1)
C(1)-C(11)-C(13)	114.6 (4)	115 (1)
C(10)-C(11)-C(12)	116.5 (4)	117 (1)
C(10)-C(11)-C(13)	111.5 (4)	111 (1)
C(12)-C(11)-C(13)	116.5 (4)	117 (1)
C(11)-C(12)-N(1)	178.6 (7)	179 (1)
C(11)-C(13)-N(2)	177.9 (6)	178 (1)
C(10)-C(13)-N(3)	176.5 (3)	177 (1)
C(10)-C(15)-N(4)	178.3 (5)	178 (1)

Solution and Refinement. Normalized structure factors were calculated in a standard way from the Wilson plot.[37] Phases were assigned to the 230 E's greater than 1.5 by the interative application of Sayre's equation.[38] The most consistent set of phased E's were used to compute an E-map which revealed 18 of the 20 nonhydrogen atom positions.[39] A subsequent electron density map was calculated with phases of the 18 atom fragment and the two remaining atom positions were disclosed. Full-matrix least-squares refinements (222 parameters) on $\Sigma w \| F_o | - | F_c \|^2$, where $w = (1/\sigma[F])^2$, with anisotropic temperature parameters reduced the conventional weighted and unweighted discrepancy indices to a minimum of $wR = 10.6\%$ and $R = 8.9\%$ for the observed reflections.[41] The scattering factors used were those of Hanson, *et al.*[40] In Table V are listed the final X-ray coordinate and thermal parameters along with their standard deviations.

The final bond distances and bond angles along with their standard deviations are listed in Tables VI and VII, respectively.[42] In Figure 3 the final computer generated X-ray model is shown. Figure 4 is the computer generated unit cell drawing of the X-ray structure.[43] Table VIII contains the observed and calculated structure factors.[44]