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THE STEREOCHEMISTRY OF BICYCLO[3.2.1]OCTANE—XVII[1]

LONG RANGE INTERNUCLEAR SPIN INTERACTIONS BETWEEN PROTONS IN DERIVATIVES OF BICYCLO[3.2.1]OCTENE-2

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Abstract—The NMR spectra at 60 and 100 MHz of several derivatives of bicyclo[3.2.1]octene-2 have been analysed by spin spin decoupling to yield the long range coupling constants. For example, in 3-bromobicyclo[3.2.1]octene-2 (V), five distinct long range interactions between protons were detected; two W-plan (*exo*-C_4—H with *exo*-C_6—H; *endo*-C_4—H with *anti*-C_8—H), one homoallylic (C_2—H with *anti*-C_8—H) and two vinyl-allylic couplings (C_2—H with *exo* and *endo* C_4—H). However, such coupling is remarkably dependent on substitution. Correlations between coupling constants and substitution are discussed and rationalized in terms of distortion of the bicyclo[3.2.1]octene-2 skeleton.

INTRODUCTION

Preliminary results have indicated that derivatives of bicyclo[3.2.1]octane are well suited for the investigation of long range coupling between protons as a function of the nature and disposition of the interjoining bonds. In particular, the bicyclo[3.2.1]-octene-2 skeleton (I) fulfils many of the desiderata for suitability as it appears to be rigid yet strain-free, possesses a small number of protons, which in appropriate derivatives, display well separated and assignable chemical shifts.[2] Indeed, from inspection of a Dreiding model[3] of 3-bromobicyclo[3.2.1]octene-2 (V), to take a simple derivative of I as an illustration, at least three kinds of long range coupling are expected. These are W-plan[4] (A with E, and Z with G), homoallylic* (B with E), and vinyl-allylic coupling (B with Z and B with A), which altogether comprise five possible remote couplings within the compass of the same molecule (Fig. 1).

We have previously reported that *exo*-4-substituted derivatives of V (e.g. II and IV) exhibit only two of the expected long range interactions (A with E, and B with E).[5] Further, we tentatively suggested that the disappearance of vinyl-allylic coupling is due to distortion of the cyclohexene ring by intramolecular dipolar repulsions.[6] In the present paper we have extended our earlier work by examining other derivatives of bicyclo[3.2.1]octene-2 by the application of the method of spin decoupling to test the above suggestion. At the same time, the results provide proofs of structure of certain derivatives of I which were produced in reactions where the stereochemical

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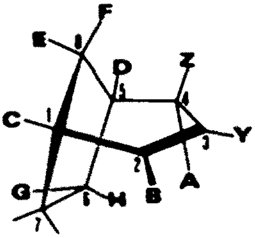
* Homoallylic coupling refers to coupling between vinyl and homoallylic protons without specifying the number of intervening bonds.

course was crucial, viz. (i) the addition of monohalocarbene to norbornene;[7] (ii) the photohalogenation of bicyclo[3.2.1]octene-2[8] and (iii) the reduction of *exo*-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 with lithium aluminum deuteride.[1]



I			
II			Y = Z = Br
III			Y = Br, Z = OH
IV	C = Me,		Y = Z = Br
V			Y = Br
VI		D = Me,	Y = Br
VII		D = Me,	Y = Br, Z = Deut
VIII	C = Me,		Y = Br, Z = Deut
IX		D = Me,	Y = Br, Z = OH
X	C = Me		Y = Br, Z = OH
XI			Z = Cl
XII			Z = Br

Letters A–Z designate protons except where C, D, Y and Z are replaced by substituents

FIG. 1 Derivatives of bicyclo[3.2.1]octene-2.

RESULTS

The NMR spectra of compounds II–XII (Fig. 1) were obtained at 60 and 100 MHz and analysed by spin decoupling. Both field and frequency sweep methods were used according to previously described procedures.[5,9]

Spectral analysis in II–X was considerably facilitated by the presence of the Br substituent at C_3 which isolates the vinyl (B) and allylic (A) protons from each other so that their resonances are not unduly complicated. It was found, contrary to expectation, that vinyl-allylic coupling was not observable in the first three compounds (II–IV), but that the vinyl (B) and allylic (A) protons individually coupled to the equatorial methylene bridge proton (E).

The replacement of the *exo* C_4 allylic substituent by a non-polar substituent, such as hydrogen or deuterium (as in V and VII) brings about a striking change in the appearance of the vinyl resonance. The signal at 6·11 ppm of V appears as a doublet of pentuplets thereby indicating that the vinyl proton (B) interacts with four other protons (Fig. 2a). In other words, *both* allylic protons (A and Z) exhibit coupling to the vinyl proton B.

Apart from the vinyl signal, the only other clear features of the spectrum of V are the signals due to the allylic protons A and Z which show signals characteristic of geminal protons in a 6-membered ring. They show as a doublet of broad and indistinct multiplets centered at 2·64 ppm (^2J = 17·0 Hz) and another doublet of narrow multiplets centered at 2·06 ppm (^2J = 17·0 Hz). Fortunately, the downfield (2.89 ppm) and upfield (1·98 ppm) branches respectively of each of these two doublets could be obtained sufficiently well resolved so that their constituent couplings could be perceived. Couplings of 4·7, 2·4 and 2·0 Hz are easily discerned in the broad branch at 2·89 ppm (Fig. 3a); and couplings of 2·0, 1·0 and 0·6 Hz are distinctly seen in the narrow branch at 1·98 ppm (Fig. 3b). The analysis and identification of these constituent couplings and the appropriate chemical shifts of the protons responsible were accomplished by double irradiation using the field-sweep method.[5]

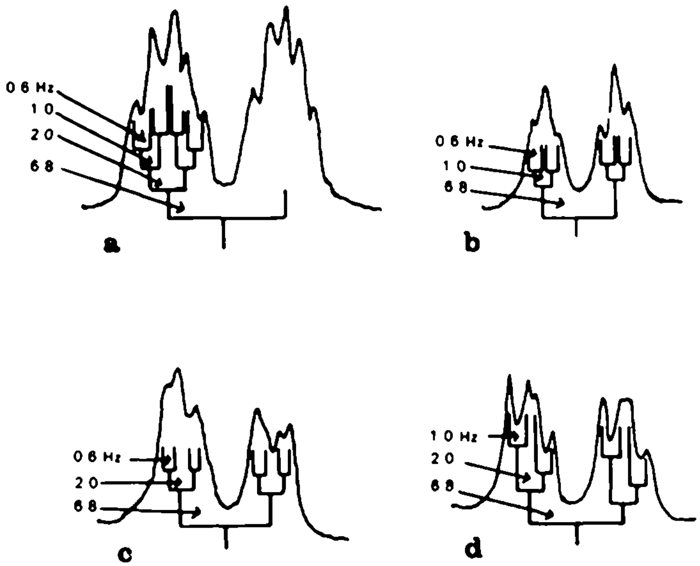


FIG. 2 Simplification of the vinyl resonance (B) of V at 100 MHz.
(a) normal spectrum; (b) on irradiation at 2·64 ppm {Z}; (c) on irradiation at 2·06 ppm {A}; (d) on irradiation at 1·37 ppm {E}.

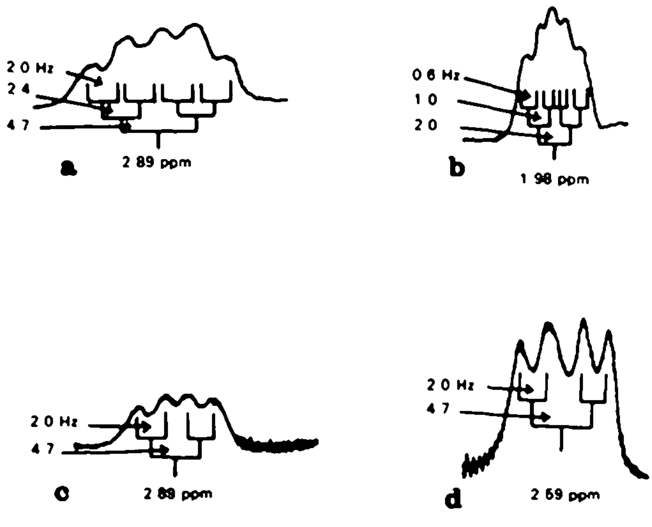


FIG. 3 Resonances of the allylic protons (A and Z) of V at 100 MHz.
(a) downfield branch of doublet due to Z; (b) upfield branch of doublet due to A; (c, d) simplification of downfield and upfield branches of the doublet due to Z on irradiation at 1·74 ppm {G}.

Informative simplification of the vinyl signal occurs on irradiating the geminal protons A and Z. Irradiation at 2·64 ppm produces a doublet of triplets with loss of the 2·0 Hz coupling (Fig. 2b), whereas decoupling of the other geminal proton by irradiation at 2·06 ppm annihilates the 1·0 Hz coupling (Fig. 2c). Therefore, it can be concluded that J_{BA} = 1·0 or 2·0 Hz and J_{BZ} = 2·0 or 1·0 Hz. The remaining coupling of 0·6 Hz in the vinyl multiplet was removed by irradiation at 1·37 ppm. (Fig. 2d). From previous experience,[5] it is known that the equatorial C_8- proton E absorbs in this region, accordingly, J_{BE} = 0·6 Hz.

The problem of assigning the chemical shifts of A and Z and the associated problem of assigning the vinyl-allylic couplings of 1·0 and 2·0 Hz were resolved by observing the resonance of A or Z during irradiation of the methylene protons. Irradiation at 1·74 ppm simplifies the signal centered at 2·64 ppm to a pair of doubled doublets by erasure of the 2·4 Hz coupling (Fig. 3c, d). The chemical shifts of the ethane bridge protons are usually found at 1·74 ppm. Therefore this 2·4 Hz coupling must be due to the interaction of G with Z, since it is only these protons which are situated on a W-arrangement of sigma bonds.[4] Consequently, the downfield doublet centered at 2·64 must be due to Z. Confirmation of this assignment is further provided by the values of the vicinal coupling constants of Z and A. The magnitudes of 4·7 and 2·0 Hz for J_{ZD} and J_{AD} are commensurate with those already found in other derivatives of bicyclo[3.2.1]octene-2.[10] Moreover, J_{AD} is usually about 2·8 Hz in II, III and IV the structures of which have been rigorously determined.

By similar procedures the coupling constants of VI and VII were extracted and assigned. The *exo*-configuration of the deuterium substituent at C_4 in VII follows firstly, from the fact that A couples with E (J_{AE} = 0·6 Hz) which requires that the interacting protons be on the ends of a W arrangement of sigma bonds[4] and secondly, from the *magnitude* of the vinyl-allylic coupling constant, 1·2 Hz.

In the case of VIII, the vinyl resonance shows as a triplet (Fig. 4a). Irradiation at 1·40 ppm (the shift for E) turns the vinyl signal into a doublet 1·2 Hz wide (Fig. 4b). However on irradiation at 2·35 ppm, (the shift for the allylic proton (A) on C_4), the triplet collapses to a doublet 1·0 Hz wide (Fig. 4c). Accordingly this small value of

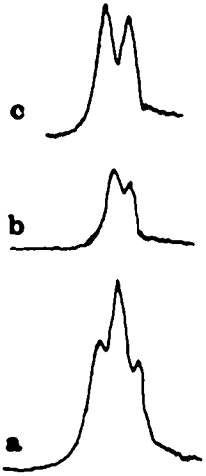


FIG. 4 (a) Resonance of vinyl proton (B) of VIII at 100 MHz; (b) irradiation at 1·40 ppm {E} leaves 1·2 Hz coupling; (c) irradiation at 2035 ppm {A} leaves 1·0 Hz coupling.

the vinyl-allylic coupling is best accommodated by *exo* placement of the deuterium substituent at C_4.

Protons in the last group of compounds (IX–XII) were decoupled by the frequency sweep method.[9] The spectral analysis of XII is typical. Characteristic features of the 100 MHz spectrum are the multiplets at 5·94 and 5·57, the broad triplet at 4·50 and the two broad resonances at 2·7 and 2·50 ppm which are due respectively to the vinyl protons B and Y, the allylic proton A and the two bridgehead protons D and C, (Fig. 5a). From their expanded spectra, the vinyl resonances were analysed into their constituent couplings without difficulty. The vinyl resonance at lower field is composed of couplings of 9·7, 6·6, 1·0 and 0·5 Hz. (Fig. 6a). The other vinyl resonance is less complex and comprises couplings of 9·7, 4·0 and 1·6 Hz (Fig. 6b). The allylic triplet remains a diffuse triplet 6·6 Hz wide on similar expansion.

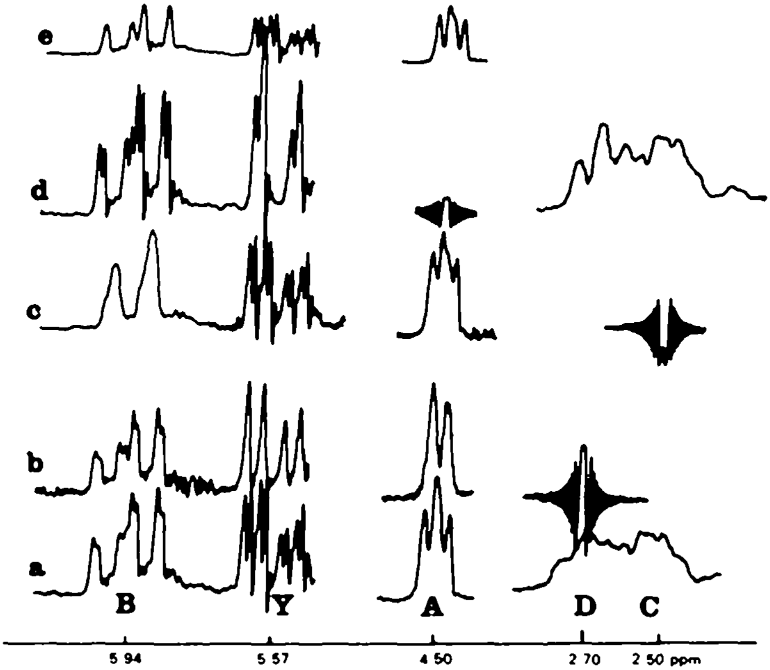


FIG. 5 (a) Main features of the normal spectrum of XII at 100 MHz; (b) irradiation at 2·7 {D}; (c) at 2·5 {C}; (d) at 4·5 {A}; and (e) at 1·38 ppm {E}.

By irradiation of the downfield bridgehead proton (at 2·7 ppm) the allylic triplet becomes a broad doublet 4·0 Hz in width (Fig. 5b). Simultaneously, the upfield vinyl resonance becomes a doublet of doublets by shedding its 1·6 Hz coupling. Therefore, the resonance at 2·7 ppm is due to D. Consequently $J_{AD} = 2{\cdot}6$ Hz, which means that A must have the *endo* configuration at C_4. The magnitude of the long range coupling (1·6 Hz) is about that expected for the geometric relation of D to Y.

Irradiation at 2·5 ppm decouples the other bridgehead proton C (Fig. 5c). This time the vinyl resonance at lower field becomes a doublet of diffuse multiplets 9·6 Hz wide, thereby showing that C couples to B with $J_{CB} = 6{\cdot}6$ Hz. The other vinyl resonance (Y) remains unaffected, therefore $J_{CY} = 0$.

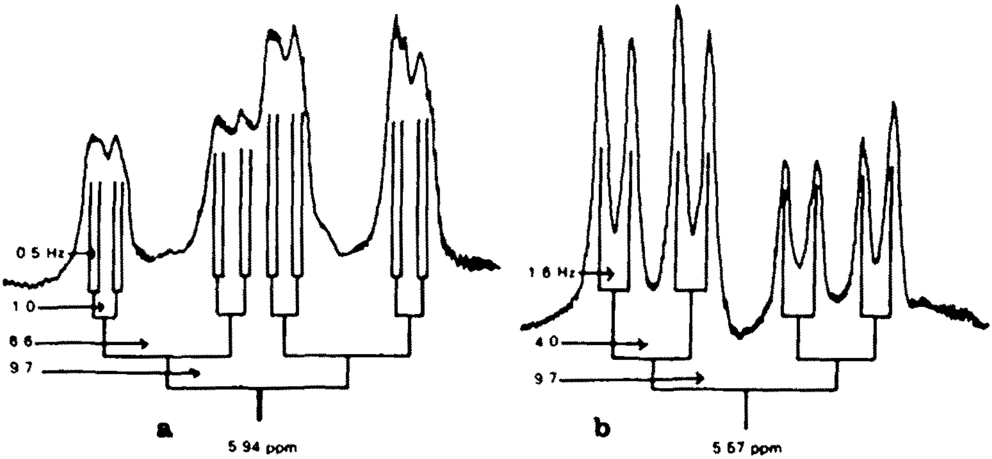


FIG. 6 Vinyl resonance B (a) and Y (b) of XII at 100 Hz sweep width at 100 MHz.

Irradiation of A (at 4·5 ppm) sharpens the signal of B by divesting it of the 0·5 Hz coupling (Fig. 5d). Decoupling of A also removes the 4·0 Hz coupling from the signal of Y leaving it as a doublet of doublets, 9·6 Hz wide. Coincidently, the diffuse signal due to the bridgehead protons becomes transformed to a triplet on the downfield side, since D now couples chiefly with E and G. A model indicates that the dihedral angles between D and the protons F and H are nearly 90°, therefore coupling between them should be negligibly small.

Irradiation at 1·38 ppm, the chemical shift for the bridge proton E, is surprisingly without much effect. The only detectable change in the overall spectrum occurs in the

TABLE 1. COUPLING CONSTANTS[a] OF DERIVATIVES OF BICYCLO[3.2.1]OCTENE-2

Compound	J_{AD}		J_{ZD}	J_{ZO}	J_{AE}	J_{BE}	J_{BZ}	J_{BA}
II	2·8				0·6	1·0		0
III	2·8				0·6	0·9		0
IV	2·8		—	—	0·4	1·4	—	0
V[a]	2·0		4·7	2·4	0·6	0·6	2·0	1·0
VI			—	2·2	0·6	0·6	2·0	1·4
VII[b]	•				0·6	0·5		1·2
VIII	•		—	—	•	1·0	—	1·2
IX	•		—	—	•	1·0	—	0
X			—	—	•	1·3		0
		J_{AY}	J_{DY}	J_{EY}				
XI[c]	2·6	4·0	1·9	0	0	1·2		0·8
XII[d]	2·6	4·0	1·6	0	0	1·0	—	0·5

• Not determined.

[a] Spectra were recorded in $CDCl_3$ except as noted. J's are absolute values in Hz.

[b] Neat.

[c] $J_{CY} = 0$, $J_{BC} = 6·3$ and $J_{BY} = 9·6$ Hz.

[d] $J_{CY} = 0$, $J_{BC} = 6·6$ and $J_{BY} = 9·7$ Hz.

signal of B which loses its 1·0 Hz coupling, accordingly, J_{EB} = 1·0 Hz, but remarkably J_{EA} and J_{EY} are essentially zero.

A similar decoupling process was carried out for *exo*-4-chlorobicyclo[3.2.1]-octene-2 (XI), *exo*-1-methyl-2-hydroxybicyclo[3.2.1]octene-3 (IX) and its allylic isomer (X). IX and X yielded only the vinyl-allylic (BA) and homoallylic (BE) coupling constants. J_{AE} could not be determined owing to broadening of the signal of A by exchange of the OH proton.

The main coupling constants of compounds II–XII which were obtained from the spin decoupling experiments are listed in the Table.

DISCUSSION

The most striking feature of the spectra of these compounds is the consistent variation in the value of the long range coupling constants with substitution. Comparison of the data of compounds II, V, VII, VIII and XII is revealing.

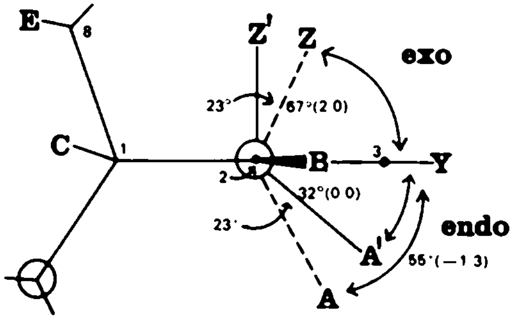
When Br is present at C_3 and C_4, then J_{BE} is 1·0 Hz (II); removal of the C_3 Br causes no change (XII), but removal of the C_4 Br drops J_{BE} to 0·5–0·6 (V, VII). On the other hand, the introduction of Me at C_1 increases J_{BE} by about the same amount, on going from II to IV and from VII to VIII (ΔJ = 0·4 Hz). It is difficult to say why this precisely happens. However, as the *exo*-C_4-Br substituent is some distance removed from the interacting EB system a steric effect seems most likely. Moreover, as the effect of substitution by Br and Me are equal and opposite, it seems reasonable to invoke buttressing of C_8 from opposite sides in the two cases as the origin of the effect.

At one time it was thought that the presence of the *exo*-Br at C_4 would play a part in relaying spin information between E and A;[11] however this does not appear to be so as J_{EA} has the same value in II and V (0·6 Hz) and even vanishes in XII.

In the matter of vinyl-allylic coupling, the rôle of polar substituents is vital. The C_4—Z and C_4—A bonds in a Dreiding model of 3-bromobicyclo[3.2.1]octene-2 (V) appear to possess the same angular relation to the plane described by B—C_2—C_3—C_4. Nonetheless, the vinyl-allylic coupling constants in V and VI are unequal in value (J_{BZ} = 2·0 and J_{BA} = 1·0 and 1·4 Hz). Substitution *exo* at C_4 by Br or OH results in the disappearance of the coupling between B and A (J_{BA} = 0 Hz for II, III, IV, IX and X). However, when deuterium is placed at the *exo* C_4 position, vinyl-allylic coupling is retained (J_{BA} = 1·2 Hz for VII and VIII).

These variations can be rationalized as follows. There is evidence from radical chemistry and electron spin resonance that the cyclohexene portion of bicyclo[3.2.1]-octene-2 (I) keeps much of the shape of the half-chair of the non-bridged molecule, so that the C_4—Z and C_4—A bonds possess *quasi*-axial and *quasi*-equatorial character.[8,12] In other words, C_1, C_2, C_3 and C_4 are coplanar and C_5 is somewhat *endo* to the plane. By making use of the empirical relation between coupling constants and the geometry of vinyl-allylic protons, a rough estimate of the shape of I can be drawn[13] (Fig. 7). By sighting along the C_2—C_4 axis it can be seen that the C_4—Z and C_4—A bonds make angles of 67° and 55° to the plane described by B—$C_2C_3C_4$. These angles correspond to values of 2·0 and −1·3 Hz for J_{BZ} and J_{BA} which are close enough to those found for compounds V and VI. Substitution on I by a single polar substituent does not change this geometry too much. However, two polar substituents cause striking changes. Thus a polar substituent C_3 and another at *exo* C_4 will repel each other by dipolar or van der Waal's forces thereby enlarging the *exo*-

dihedral angle at the expense of the *endo* angle (Z → Z′ and A → A′). Assuming a rotation of 23° the *endo* C_4–A′ bond will be swept into the null coupling sector (θ = 32°) and J_{AB} vanishes (Fig. 7) (e.g. J_{BA} = 0 for compounds II, III, IV, IX and X). Of course, a deuterium substituent at the *exo* C_4 position will not experience such repulsion; there will be no resulting distortion and consequently coupling between B and A will be about the same as that found for the *exo*-C_4 hydrogen analogue; (e.g. J_{BA} is 1·0 1·4 Hz for V, VI, VII and VIII). Similarly, a sole polar substituent *exo* at C_4 or at C_3 should make little difference to J_{BA} as the molecule will be equally free of dipolar repulsion. This is borne out by the fact that XI and XII have values of 0·8 and 0·5 Hz for J_{BA} which compare well with those encountered in the 3-bromo derivatives (cf. V, VI, VII and VIII).



V Z = A = H, Y = Br
II Z′ = Br, A′ = H, Y = Br
XII Z = Br, A = H, Y = H

FIG. 7 Distortion of the bicyclo[3.2.1]octene-2 skeleton on substitution.

Finally, it should be pointed out that the present results are in close agreement with those found for the benzo[3.4]- and benzo[6.7]bicyclo[3.2.1]octa-3,6-dien-2-yl acetates.[14] It is interesting to note that despite an olefinic or aromatic bond between C_6 and C_7 in these bicyclo[3.2.1]octene-2 derivatives, the magnitudes of the vinyl-allylic coupling constants reveal that the cyclohexene moiety is still an unflattened half-chair.

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