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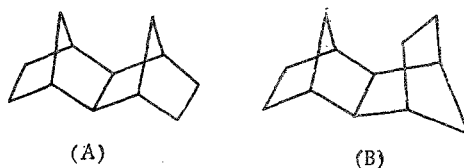
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¹³C NMR spectroscopy is widely used to establish the structure and stereochemistry of polycyclic hydrocarbons [1-3].

However literature data involving the study of the ¹³C NMR spectra of a broad class of dimers and trimers of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene (NBD)) is essentially nonexistent. Meanwhile the compounds indicated have become firmly established in synthetic usage and it is evident that the scope of their usage will continue to grow.

In this connection it is of interest to investigate the ¹³C NMR spectra of all known dimers and trimers of norbornadiene [4, 5]. The latter contain norbornane and norbornene fragments in their molecules which appreciably facilitate the reliable assignment of stereoisomers. For this type of conjugated structures there is observed an interaction of the exo-oriented substituents with the C⁷ bridge carbon atoms as a result of which there is a considerable diamagnetic shift of the signals ($\Delta\delta$ up to 4 ppm) of the latter in the ¹³C NMR spectrum [6]. This effect appears still more pronounced in the polycyclics having two norbornane fragments, for example those such as stereoisomers of tetracyclo[6.2.1.0^{2,7}.0^{3,6}]-dodecane (A, B) [1].



In the case of the endo-exo isomer (B) the difference in the chemical shifts (CS) of the signals of carbon atoms C¹¹, C¹² are as much as 8 ppm which completely unequivocally demonstrates the dependence of the chemical shifts of the bridge carbons on the spatial orientation of the substituents (cyclic ones in this instance). We used these compounds (A, B) [1] and also norbornane and norbornene [6] as models for the assignment of signals in the ¹³C NMR spectra of NBD dimers and trimers.

The ¹³C NMR spectra were recorded on a Jeol-FX-90Q spectrometer with overall proton decoupling and high resolution with partial retention of the Overhauser effect. Resolution of digital analog conversions for a 2000-Hz scan equals 0.25 Hz. Spin-spin coupling analysis (¹³C-H) will be reported in subsequent papers.

It is known that the presence of symmetry elements in the molecule decreases the number of signals in the spectrum [7]. Thus having two planes of symmetry in the molecule of endo-heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane (I) [8] reduces the number of signals from 14 atoms of carbon to five (Fig. 1). Doublet signals of double intensity in the cyclopropane region at 16.77 ppm pertain to C⁴, C⁵, C¹¹, and C¹². In a stronger field signals of C⁶ and C¹³ were found. Triplet signals at 33.52 ppm pertain to C⁷ and C¹⁴. Differences in intensity make it possible to assign signals of C¹ and C⁸ (31.86 ppm) and C², C³, C⁹, and C¹⁰ (39.98 ppm).

¹³C NMR spectral data of the saturated dimer of NBD (II) completely verify the structure proposed for it (Fig. 2) [5]. The presence of two planes of symmetry and a fourfold-mirror

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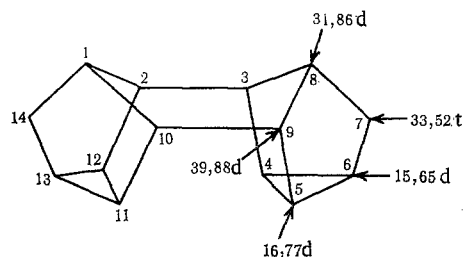


Fig. 1. Endo,endo-heptacyclo[8.4.0.0^{2,12}-0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane "Binor-S".

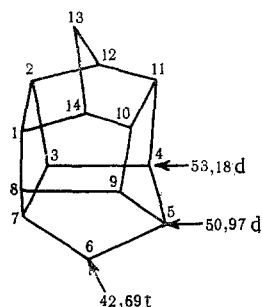


Fig. 2. Heptacyclo[6.6.0.0^{2,12}.0^{3,7}-0^{4,11}.0^{5,9}.0^{10,14}]tetradecane.

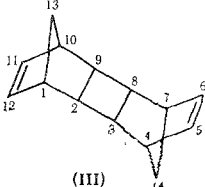
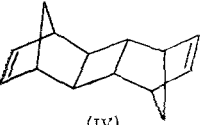
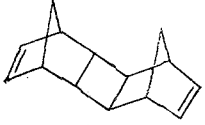
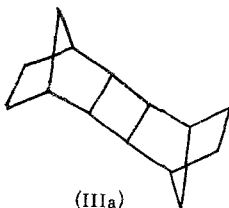
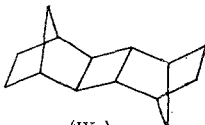
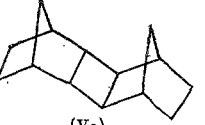
rotation symmetry axis (S_4) decreases the number of signals to three. Triplet signals at 42.69 ppm pertain to C⁶ and C¹³. Signals of double intensity (50.97 ppm) belong to C⁵, C⁷, C¹², and C¹⁴, and signals with a maximum intensity at 53.18 ppm to C¹, C², C³, C⁴, C⁸, C⁹, C¹⁰, and C¹¹.

For $[2\pi + 2\pi]$ -dimers of NBD (Table 1) containing up to two olefin bonds establishing the stereochemistry does not present any particular difficulties. In the spectra of (III) and (IV) the decrease of the general number of signals to four in the weak field spectrum indicates the high symmetry of the molecule. Doublet signals in the weak field spectrum pertain to the saturated carbon atoms, and triplet signals at 53.44 and 42.13 fit the bridge carbon atoms. The doublet at 44 ppm belongs to the junction carbon atoms. As it would be expected the most informative in the determination of exo or endo orientation of the fragments of the molecules prove to be the C¹³ and C¹⁴ carbon atoms and the carbon atoms of the cyclobutane ring. On account of this the 1,4 shielding interactions of the bridge carbon atoms with the cyclobutane substituent in the exo position results in diamagnetic shifting of the C¹³ and C¹⁴ signals in comparison with the endo position, the NBD dimer with a mp of 67-68°C has the exo-trans-exo configuration (IV) and the hydrocarbon with mp 92-93°C the endo-trans-endo configuration (III). The amount of the observed shift ($\Delta\delta = 11$ ppm) for the bridge carbon atoms is more than twice that ($\Delta\delta = 4$ ppm) for the cyclobutane fragment which evidently is explained by the amount of participation of the carbon atoms in the interaction. For the third dimer of this type (V), from the aggregate of the spectral data it uniquely conforms to the endo-trans-exo structure.

The closeness of the signals of the sp^2 hybridized carbon atoms in compounds (III) and (IV) is evidently caused by the fact that in the unsaturated derivatives as a result of orientation of the proton in the plane of the double bonds long range interactions through space are slight. For this reason the C⁵, C⁶ and C¹¹, C¹² signals coincide in the spectrum of the "hybrid" endo-trans isomer (V) in $CDCl_3$. Replacement of the solvent by C_6D_6 makes it possible to note the differences of the chemical shifts of these atoms, amounting to 0.054 ppm.

In the spectrum of the saturated dimers (IIIa)-(Va) (obtained by hydrogenation of (III-V)) new triplet signals were discovered in the strong field spectra. This calls attention to the fact of the existence of diamagnetic shifts of the signals of the bridge carbons C¹³ and C¹⁴ amounting to 10 ppm. This no less significant chemical shift of the indicated carbons in this instance is the desired criterion making it possible to deduce the orientation of the substituent. The difference between the chemical shifts of the signals of C¹³ and C¹⁴ is 10 ppm.

TABLE 1. Chemical Shifts of Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]-tetradecane-5,11-dienes and Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]-tetradecanes

Compound	δ , ppm (TMS, CDCl ₃)							
	C ^{1,10}	C ^{2,9}	C ^{3,8}	C ^{4,7}	C ^{5,6}	C ^{11,12}	C ¹³	C ¹⁴
 (III) endo-trans-endo	44,95d	43,78d	43,78d	44,95d	137,8d	137,8d	53,44t	53,44t
 (IV) exo-trans-exo	44,08d	39,70d	39,70d	44,08d	135,93d	135,93d	42,13t	42,13t
 (V) endo-trans-exo	45,04d	41,05d	40,90d	44,21d	135,86d	135,86d	53,34t	43,95t
 (IIIa) endo-trans-endo	39,96d	39,05d	39,05d	39,96d	24,19t	24,19t	43,00t	43,00t
 (IVa) exo-trans-exo	38,79d	45,38d	45,38d	38,79d	27,74t	27,74t	33,50t	33,50t
 (Va) endo-trans-exo	40,09d	42,69d	41,39d	38,92d	27,87t	23,84t	41,26t	33,42t

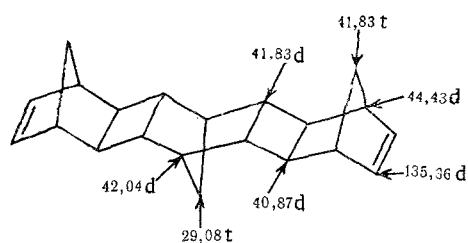


Fig. 3. exo-trans-exo-trans-exo-Octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]-heneicosa-5,14-diene.

TABLE 2. Chemical Shifts of Hexacyclo[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradec-12-enes and Hexacyclo[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradecanes

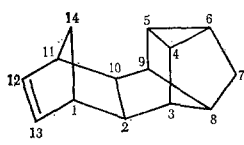
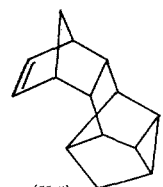

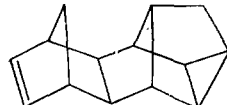
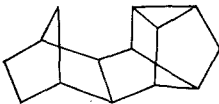
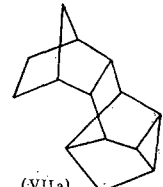
Compound	δ , ppm (TMC, CDCl ₃)								
	C ^{1,11}	C ^{2,10}	C ^{3,9}	C ^{4,5}	C ⁶	C ⁷	C ⁸	C ^{12,13}	C ¹⁴
 (VI) exo-endo	41.03 d	45.03 d	42.52 d	12.83 d	18.64 d	28.65 t	47.46 d	140.31 d	42.43 t
 (VII) endo-exo	48.98 d	45.77 d	44.34 d	18.33 d	13.48 d	32.55 t	36.97 d	136.19 d	52.56 t
 (VIII) endo-endo	47.25 d	45.38 d	45.38 d	14.13 d	20.11 d	27.31 t	48.63 d	133.16 d	57.48 t
 (IX) exo-exo	49.30 d	45.12 d	44.77 d	18.16 d	14.30 d	33.77 t	39.07 d	138.50 d	43.39 t
 (VIa) exo-endo	37.62 d	49.15 d	47.25 d	12.66 d	16.95 d	28.09 t	43.73 d	30.86 t	34.63 t
 (VIIa) endo-exo	40.40 d	49.20 d	42.82 d	18.20 d	13.70 d	33.46 t	37.62 d	24.58 t	42.17 t

TABLE 2 (continued)

Compound	δ , ppm (TMS, CDCl_3)								
	$\text{C}^{1,11}$	$\text{C}^{2,10}$	$\text{C}^{3,9}$	$\text{C}^{4,5}$	C^6	C^7	C^8	$\text{C}^{12,13}$	C^{14}
 (VIIIa) endo-exo	41,26 d	47,64 d	46,03 d	13,66 d	13,83 d	27,44 t	50,02 d	26,05 t	46,86 t
 (IX) exo-exo	39,95 d	52,55 d	46,25 d	16,68 d	11,59 d	33,45 t	38,39 d	30,41 t	35,49 t

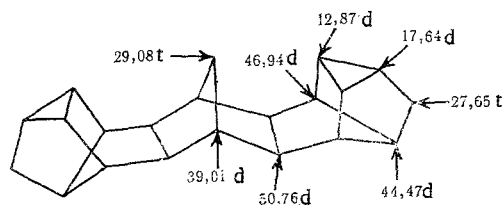


Fig. 4. endo-exo-endo-Decacyclo[9.9.1.0^{2,10}.-0^{3,8}.0^{4,6}.0^{5,9}.0^{12,20}.0^{13,19}.0^{14,16}.0^{15,18}]-heneicosane.

A similar effect is observed for the series of stereoisomers of the hexacyclic dimers of NBD (VI)-(IX) (Table 2) the identification of which is made on the basis of the multiplicity, the intensity, and the value, of the chemical shift. It should be noted that the analysis of the spectra of (VI)-(IX) is made somewhat easier by the fact that the structure of (VI) has been completely and unequivocally established by x-ray methods [9].

As a result of stronger intramolecular steric hindrances in the hydrocarbons in question diamagnetic shifts of signals of the carbon atoms are encountered more frequently and might be explained by either 1,4 or δ interactions which show up in many of the shielding of the C^{14} bridge atoms of compounds (VI), (VIa), (IX), and (IXa) in contrast to the corresponding carbon atoms in (VII), (VIIa), (VIII), and (VIIIa). We found more significant shifts ($\Delta\delta = 10$ ppm) also in the C^4 and C^5 carbons of the cyclopropane ring in the exo-endo and endo-endo isomers and at the junction atom C^8 in the endo-exo and exo-exo isomers. The ^{13}C NMR spectral data verify the proposed structures [4, 5] for each of the NBD isomers.

Results of investigations of the ^{13}C NMR spectra of the NBD dimers and the establishment thereby of the governing principles made it possible to determine the structures of two NBD trimers (X) and (XI) described in the literature (Fig. 3, 4).

The decrease in the total number of signals in the spectrum of (X) to seven and the relationship of their intensities testify to the high symmetry of the molecule. From the analysis of the chemical shifts of the bridge carbon atoms C^{19} and C^{21} (41.83 ppm) of the trimer it follows that the norbornene fragment has the exo configuration and a significant diamagnetic shift of the C^{20} signals (29.08 ppm) is created by the presence of two cyclic substituents in the exo position. Thus trimer (X) is the exo-trans-exo-trans-exo isomer.

In the spectrum of trimer (XI) all eight signals were found, the chemical shifts and multiplicities of which correspond to a compound of the nortricyclo type. A strong shift of the signals of the C²¹ bridge carbon (29.08 ppm) is most probably caused by the fact that the central norbornene fragment has only exo substituents on both sides.

The values of the chemical shifts of C⁴, C⁵, C¹⁴, C¹⁵ carbon atoms (12.87 ppm) indicate the endo orientation of the side fragments of the molecule which makes it possible to ascribe the endo-exo-endo structure to (XI).

CONCLUSIONS

We have obtained the ¹³C NMR spectra of all known dimers and trimers of norbornadiene. We have determined the principles governing the changes in chemical shifts depending on the orientation interactions of the fragments and carried out the stereochemical assignment of all known isomers. We have shown the agreement of the configurations of the latter determined by the ¹³C NMR method with their structures previously established by other methods.

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