^{1}H and ^{13}C NMR spectra of polycyclic compounds
7.* Stereochemical identification of a mixture of five stereoisomeric norbornadiene trimers

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Using 2D ^{1}H and ^{13}C correlation NMR spectroscopy, all signals in the ^{1}H and ^{13}C NMR spectra of five stereoisomeric bicyclo[2.2.1]heptadiene trimers, decacyclo$[9.9.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}.0^{12,20}.0^{13,18}.0^{14,16}.0^{15,19}]$heneicosanes, obtained by Pd-catalyzed codimerization of norbornadiene dimer with quadricyclane followed by homocyclotrimerization of the latter were assigned unambiguously. Independent stereochemical identification of the trimers was performed using data on the nuclear Overhauser effect.

Key words: norbornadiene, bicyclo[2.2.1]heptadiene trimers, stereoisomers, ^{1}H and ^{13}C NMR spectra, 2D NMR spectroscopy.

Strained polycyclic compounds built of three-, four-, and five-membered cycles possess unique physicochemical properties which are mostly dependent on their spatial structure.[2–7] Among these compounds, bicyclo[2.2.1]heptadiene (norbornadiene, NBD) trimers with two nortricyclane fragments **1**—**10** are of particular interest. The synthesis of NBD trimers **1**, **2** by condensation of NBD dimer, *endo-exo*-hexacyclo$[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]$tetradec-12-ene, with quadricyclane under the action of Pd-containing catalysts was described.[8] Trimers **1** and **2** are formed along with three isomeric trimers **5**—**7** which are the products of competing quadricyclane homocyclotrimerization. According to GLC data, the ratio of **1** : **2** : **5** : **6** : **7** stereoisomers in the five-component mixture is 10 : 7 : 10 : 6 : 5.

Previously,[6] we studied the ^{13}C NMR spectra of individual compounds **5**—**7** and established their structure and stereochemistry. Attempts to separate the mixture obtained[8] into individual components by GLC and HPLC failed; therefore only the chemical shifts (CS) in the ^{13}C NMR spectra of isomers **1** and **2** measured in the five-component mixture were reported.[8] Because of the low operating frequency of the spectrometer (22.5 MHz) the signals for each carbon atom of compounds **1**, **2**, and **5**—**7** were unresolved, which made the assignment of signals difficult, especially in the region of δ from 38 to 48, where stereochemically important signals of the C(21), C(18), and C(8) atoms are observed. It was impossible to avoid errors in assigning the signals even by using reference data.[9,10]

In this work, the problem of complete and unambiguous assignment of all ^{1}H and ^{13}C NMR signals of five stereoisomers of norbornadiene trimers (see Ref. 8) was solved by 1D and 2D high-resolution NMR spectroscopy. Independent stereochemical identification of five isomers (**1**, **2**, and **5**—**7**) out of ten theoretically possible ones was also carried out using direct observation of nuclear Overhauser effects for spatially close protons.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a VXR-500 spectrometer operated at a frequency of 500 MHz for ^{1}H and 125 MHz for ^{13}C nuclei. Two-dimensional ^{1}H—^{1}H COSY spectra with phase-sensitive detection were recorded using the standard DISRNMR-94 procedure. Heteronuclear 2D CHCORR correlation spectra including 2D CHCORR LONG RANGE (CHCORRLR) ones were recorded using an inversion probe. Two-dimensional NOESY spectra were recorded with a mixing time of 120 μs and with $CDCl_3$ as solvent.

Norbornadiene trimers 1 and 2 were synthesized following the known procedure[8a] by cocondensation of the NBD dimer, *endo-exo*-hexacyclo$[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]$tetradec-12-ene,[8b] with quadricyclane in the presence of zero-valence palladium

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* For Part 6, see Ref. 1; for Parts 1—5, see Refs. 2—6.

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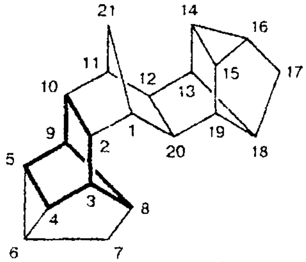
complex $Pd(PPh_3)_4$[8c] under conditions of competing quadricyclane homocyclotrimerization resulting in the formation of trimers 5—7.[8a]

Results and Discussion

Stereochemical diversity of conceivable diastereomers of norbornadiene trimers with two deltacyclane fragments (**1**—**10**) is due to different types of joining of the three norbornane (NB) fragments that can be distinguished in the trimer molecule. For clarity, one of them in the molecule of *exo-endo-exo-endo*-decacyclo-[9.9.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{12,20}$.$0^{13,18}$.$0^{14,16}$.$0^{15,19}$]heneicosane (**1**) is shown by a bold line. Ten nondegenerate stereoisomers can be grouped by type of joining of the central and the side NB fragments, as is shown in Fig. 1.



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Trimers **1**—**10** contain magnetically nonequivalent atoms, namely, 14 carbon and 15 hydrogen atoms for the molecules with one symmetry plane and 8 carbon and 8 hydrogen atoms for those with two symmetry planes. Fifty-six individual signals were found in the 1D ^{13}C NMR spectrum, which does not contradict the existence of five stereoisomers in the mixture (58 nonequivalent carbon atoms). Two pairwise coinciding signals (at δ 16.84 and 39.00) differ in the correlation peaks in the 2D CHCORR spectrum (Table 1). We preliminarily assessed the structure and stereochemistry of the mixture components using the reported data[6]; however, it was impossible to unambiguously eliminate the signals of isomers **5**—**7** and to refine the spectral assignment for isomers **1** and **2** because of the too close CS values of the resonance signals, differing by less than 0.05 ppm. A rather complicated one-dimensional ^{1}H NMR spectral pattern makes it possible to unambiguously assign only some signals, namely, to distinguish two pairs of signals of the H(21), H(21′) geminal protons of isomers **1** and **2** at δ 0.96 and 2.40 (J_{gem} = −9.9 Hz) and at δ 0.99 and 1.86 (J_{gem} = −10.4 Hz), respectively. These signals become the starting point for distinguishing the proton systems of compounds **1** and **2** that have one symmetry plane. Two-dimensional spectra are more informative and make it possible to distinguish a set of signals of C and H atoms with common proton—

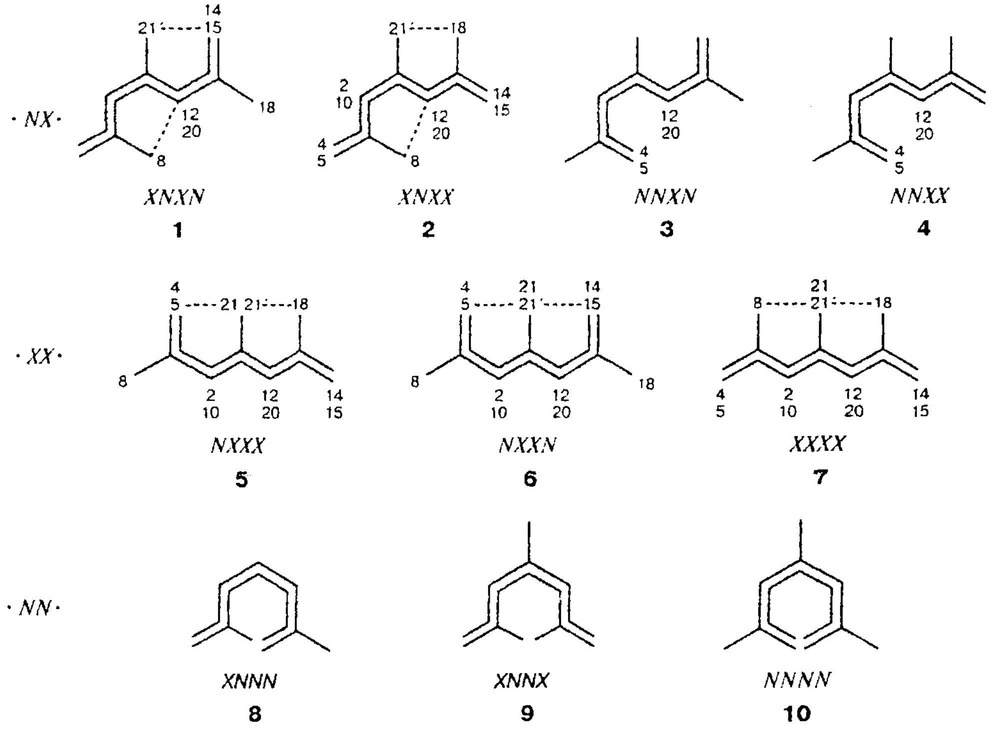

Fig. 1. Schematic representation of stereoisomeric NBD trimers **1**—**10** with two deltacyclane fragments in the symmetry plane of the molecules and informative NOESY cross-peaks. Notations: *N* is *endo* and *X* is *exo*.

Table 1. Parameters of ^{1}H, ^{13}C, ^{1}H—^{1}H COSY, NOESY, 2D CHCORR, and 2D CHCORRLR NMR spectra (CDCl$_3$, δ, J/Hz) of stereoisomeric NBD trimers **1**, **2**, and **5**—**7** with two deltacyclane fragments

Compound	C, H atoms	δ ^{13}C	δ ^{1}H	Cross-peaks		
				^{1}H—^{1}H COSY	NOESY	CH, direct and long-range
1	1, 11	41.67	2.15 (br.s)	2.40, 2.19, 1.97, 1.91, 1.76, 0.96		2.15, 0.96
	2, 10	50.73	2.20—2.16 (m)	2.40, 2.15, 1.52	1.79, 1.03, 0.96, 0.78	2.19, 0.96, 1.79, 1.97, 2.14, 2.40
	3, 9	42.63	1.79 (br.s)	2.15, 1.97, 0.78	2.19, 2.10	1.79, 0.96, 1.03, 1.52
	4, 5	18.44	0.79—0.77 (m)	1.79, 1.03	2.19	0.78, 1.52, 1.79, 2.19
	6	13.35	1.01—1.06 (m)	1.52, 0.78	2.19	1.03, 1.52
	7	33.73	1.52 (br.s)	2.19, 1.97, 1.03		1.52, 0.78, 1.03
	8	38.61	1.97 (br.s)	2.15, 1.79, 1.52	2.10	1.97, 0.78, 1.03, 1.52, 2.19
	12, 20	43.08	2.10 (br.s)	1.91, 0.96	1.97, 1.79, 1.66	2.10, 0.96, 1.91, 2.14, 2.19
	13, 19	47.64	1.91 (br.s)	2.15, 2.10, 1.66, 0.79	1.31	1.91, 0.79, 1.30
	14, 15	13.53	0.83—0.79 (m)	1.91, 1.66, 1.22	2.40, 1.31	0.79, 1.30, 1.66, 2.10
	16	16.84	1.25—1.20 (m)	1.31, 0.79		1.22
	17	29.09	1.31 (t, J = 1.4)	1.66, 1.22	1.91, 0.79	1.31, 1.22
	18	43.90	1.66 (m)	1.91, 1.31, 0.79	2.10	1.66, 0.79, 1.30, 2.10
	21	38.27	0.96 (d, J = −9.9; t, J = 1.2)	2.40, 2.15, 2.10	2.19	0.96
	21′		2.40 (d, J = −9.9; d, J = 1.8)	2.19, 2.15, 0.96	0.79	2.40, 2.10
2	1, 11	41.41	1.99 (br.s)	2.15, 1.86, 0.99	1.84, 1.73	1.99, 0.99
	2, 10	50.77	2.15 (br.s)	2.27, 1.98, 0.99, 0.78	1.84, 0.99	2.15, 0.99, 1.84, 1.98
	3, 9	42.69	1.84 (br.s)	2.27, 0.78	1.99, 1.55, 2.15	1.84, 0.78, 1.04, 1.55
	4, 5	18.55	0.79—0.77 (m)	2.27, 2.15, 1.84, 1.04		0.78, 1.55, 1.84, 2.27
	6	13.36	1.01—1.06 (m)	1.55, 0.78		1.04, 1.55
	7	33.72	1.55 (br.s)	2.27, 1.04	1.84	1.55, 0.78, 1.04
	8	38.74	2.27 (br.s)	2.15, 1.84, 1.55, 0.78	2.15, 1.84	2.27, 0.78, 1.04, 1.55, 1.84, 2.14
	12, 20	47.30	2.15 (br.s)	2.18, 1.99	1.84, 1.73, 0.82	2.15, 0.82, 0.99, 1.73
	13, 19	46.33	1.73 (m)	0.82	2.18, 2.15, 1.99, 1.45	1.73, 0.82, 0.91, 1.45
	14, 15	16.84	0.79—0.83 (m)	2.18, 1.73, 0.91	2.15	0.82, 1.45, 1.73, 2.14
	16	11.50	0.94—0.89 (m)	1.45, 0.82		0.91, 1.45
	17	33.68	1.45 (br.s)	2.18, 0.91	1.73	1.45, 0.82, 0.91
	18	40.39	2.20—2.16 (m)	1.73, 1.45, 0.82	1.86, 1.73	2.18, 0.91, 1.45, 2.14
	21	39.04	0.99 (d, J = −10.4; t, J = 1.2)	2.15, 1.98, 1.86	2.15	0.99
	21′		1.86 (d, J = −10.4; t, J = 1.8)	1.98, 0.99	2.18	1.86, 2.14
5	1, 11	44.09	1.99 (br.s)	2.12, 1.93, 1.73, 1.46	1.83, 1.76, 1.73	1.99, 0.75, 0.78, 2.00
	2, 10	49.77	1.76 (m)	1.93, 1.46	1.99, 1.73, 1.70	1.76, 1.93, 1.98, 2.12
	3, 9	46.97	1.93 (br.s)	1.99, 1.76, 1.70, 0.75	1.27	1.93, 0.75, 1.27, 1.76, 1.98
	4, 5	12.77	0.75 (d, J = 4.9; q, J = 1.8)	1.93, 1.70, 1.24	2.12	0.75, 1.27, 1.70, 1.93
	6	17.89	1.25—1.20 (m)	1.27, 0.75		1.24, 1.27
	7	27.58	1.28—1.26 (m)	1.70, 1.24	1.93	1.27, 1.24
	8	43.92	1.70 (m)	1.93, 1.27, 0.75	1.76	1.70, 0.75, 1.24, 1.27
	12, 20	54.35	1.73 (m)	2.12, 1.99, 1.46	1.99, 1.84, 1.76, 0.78	1.73, 1.76, 1.83, 1.98
	13, 19	45.86	1.84 (br.s)	2.21	1.99, 1.73, 1.47	1.84, 0.78, 1.47, 1.73, 2.12
	14, 15	17.23	0.79—0.77 (m)	2.21, 0.92	1.73, 1.47	0.78, 1.47, 1.73, 2.21
	16	11.65	0.94—0.89 (m)	1.47, 0.78		0.92, 1.47, 2.21
	17	33.70	1.47 (br.s)	2.21, 0.92	1.84, 0.78	1.47, 0.92
	18	39.00	2.21 (br.s)	1.84, 1.47, 0.78	1.46	2.21, 0.92, 1.47, 1.83
	21	30.12	2.13—2.11 (m)	1.99, 1.73, 1.46	0.75	2.12, 1.72, 1.76, 1.98
	21′		1.46 (d, J = −9.6)	2.12, 1.99, 1.76, 1.73	2.21	1.46

(*to be continued*)

Table 1 (*continued*)

Compound	C, H atoms	δ ^{13}C	δ ^{1}H	Cross-peaks		
				^{1}H—^{1}H COSY	NOESY	CH, direct and long-range
6	1, 11	39.00	2.13—2.09 (m)	1.67		2.12, 0.81, 1.73, 2.12
	2, 10, 12, 20	50.75	1.67 (t, J = 2.1)	2.12, 1.94	1.73	1.67, 1.94, 2.12
	3, 9, 13, 19	46.94	1.94 (br.s)	1.73, 1.67, 0.81	1.28	1.94, 0.81, 1.22, 1.28, 1.67, 2.12
	4, 5, 14, 15	12.88	0.83—0.79 (m)	1.94, 1.73, 1.24	2.12	0.81, 1.28
	6, 16	17.65	1.25—1.20 (m)	1.28, 0.81		1.24, 1.28
	7, 17	27.66	1.28—1.26 (m)	1.73, 1.24	1.94	1.28, 0.81, 1.24
	8, 18	44.45	1.74—1.72 (m)	1.94, 1.28, 0.81	1.67	1.73, 0.88, 1.24, 1.28
	21, 21′	29.10	2.13—2.09 (m)	1.67	0.81	2.12, 1.67
7	1, 11	43.81	1.84 (br.s)		2.15, 1.49	1.84, 1.79, 2.14
	2, 10, 12, 20	53.54	1.84 (br.s)	2.15, 1.49, 0.78	2.15	1.84, 1.49, 1.79, 1.84
	3, 9, 13, 19	45.77	1.79 (br.s)	2.15, 0.78	1.45	1.79, 0.91, 1.45
	4, 5, 14, 15	17.03	0.79—0.77 (m)	2.15, 1.84, 1.79, 0.45, 0.91		0.78, 1.45, 1.79, 2.14
	6, 16	11.36	0.94—0.89 (m)	0.78, 1.45	1.45	0.91, 1.45
	7, 17	33.63	1.45 (br.s)	2.15, 0.91	1.79, 0.78 0.91	1.45, 0.91
	8, 18	38.95	2.15 (br.s)	1.84, 1.79, 1.45, 0.78	1.49, 1.84	2.15, 0.91, 1.45, 1.84
	21, 21′	31.22	1.49 (br.s)	1.84	2.15, 1.84	1.49, 1.84

proton and proton—carbon spin-spin coupling constants (SSCC) for each of the five isomers.

The 2D ^{1}H—^{1}H COSY spectrum of compound **1** contains 15 groups of protons unambiguously belonging to the same system (Scheme 1, the data are given in ppm).

Correlation of these signals with the signals of carbon atoms in the 2D CHCORR spectrum made it possible to assign the CS of carbon atoms, confirmed by the 2D experiment with long-range CH-constants in the 2D CHCORRLR spectrum (see Table 1). An *endo-exo*-position (· *NX* ·) of the side NB fragments at the central NB fragment in isomer **1** was determined using the close CS values of the signal of the C(21) atom (38.27 ppm) and the analogous signal of tricyclopentadiene,[11] which has a similar type of joining of the norbornene and cyclopentene fragments at the norbornane skeleton of the molecule. The signals of the C(14) and C(15) atoms of the cyclopropane fragment at δ 13.53 are also stereochemically informative; they indicate the *endo*-substitution (· · · *N*) of the right NB fragment, since these atoms are shielded as compared with the C(4) and C(5) atoms (their signals are observed at δ 18.44) because of steric compression upon interaction with the bridging C(21) atom. Additionally, stereochemically informative is the signal of the C(16) atom (at δ 16.84), deshielded because of the electron density redistribution. Similarly, the *exo*-substitution (· · · *X*) of the left NB fragment results in shielding of the C(8) atom (the signal at δ 38.61) compared with the C(18) atom (the signal at δ 43.90) due to interaction with the C(12) and C(20) atoms (the signal at δ 43.08) and to the alternation of the CS values for the C(7) (at δ 33.73) and C(17) (at δ 29.09) atoms of the same type. Unambiguous confirmation of our stereochemical assignments was obtained in the 2D NOESY experiment (Fig. 2), in which the informative cross-peaks at δ 2.40 (H(21′)) — 0.79 (H(14, 15)) and 1.97 (H(8)) — 2.10 (H(12, 20)) are observed. This made it possible to assign the *XNXN* structure to isomer **1**. It should be noted that the *NNXN* structure of isomer **3** was ruled out since no cross-peak at δ 0.78 (H(4, 5)) — 2.10 (H(12, 20)) is observed in the 2D NOESY spectrum.

Scheme 1

0.96 (H(21)) → 2.10 (H(12, 20)) → 1.91 (H(13, 19)) → 1.66 (H(18)) → 1.31 (H(17)) → 1.22 (H(16)) → 0.79 (H(4, 5))
↑↓
2.40 (H(21′)) → 2.19 (H(2, 10)) → 2.15 (H(1, 11)) → 1.79 (H(3, 9)) → 0.78 (H(4, 5)) → 1.03 (H(6)) → 1.52 (H(7)) →
→ 1.97 (H(8))

The proton system of compound **2** with one symmetry plane is characterized by 14 nonequivalent signals since two groups of anisochronal (H(2), H(10) and H(12), H(20)) protons that are indistinguishable under the experimental conditions have signals at δ 2.15. (The signals of indistinguishable H(1) and H(11) protons in isomer **1** are also observed at δ 2.15.) This is indicated, *e.g.*, by the cross-peaks at δ 2.15 (H(2, 10)) — 2.27 (H(8)) and at δ 2.15 (H(12, 20)) — 2.18 (H(18)) due to the coupling with protons in distant molecular fragments (see the 2D ^{1}H—^{1}H COSY spectrum). The characteristic cross-peaks at δ 1.86 (H(21′)) — 2.18 (H(18)) and at δ 2.27 (H(8)) — 2.15 (H(12, 20)) in the 2D NOESY spectrum, as well as the more low-field CS of the signals of the C(4) and C(5) atoms (δ 18.55) and the C(14) and C(15) atoms (δ 16.86) compared to those of the C(6) and C(16) atoms (δ 13.36 and 11.50, respectively), indicate the *XNXX*-configuration of isomer **2**. For isomer **4** having a similar stereochemistry with the *NNXX*-configuration the interaction between the H(12, 20) and H(4, 5) atoms should be observed in 2D NOESY experiment.

The key signals at δ 2.12 and 1.46 (the H(21) and H(21′) atoms, respectively, J_{gem} = −9.6 Hz) of the proton system of compound **5** are less illustrative as compared to analogous signals of isomers **1** and **2**, since they are overlapped by the signals of other protons also observed in the same region. However, the NOE cross-peaks at δ 1.46 (H(21′)) — 2.21 (H(18)) and at δ 2.12 (H(21)) — 0.75 (H(4, 5)) unambiguously indicate the *endo*-*exo*-joining (*NX*· ·) of the left and central NB fragments and the *exo*-*exo*-joining (· · *XX*) of the central and right NB fragments. Additionally, the NOE cross-peaks at δ 0.78 (H(14, 15)) — 1.73 (H(12, 20)) and at δ 1.76 (H(2, 10)) — 1.70 (H(8)) confirm the *NXXX*-joining in isomer **5**.

The proton systems of compounds **6** and **7** indicate that these molecules have two symmetry planes each. The cross-peaks at δ 2.12 (H(21, 21′)) — 0.81 (H(4, 5, 14, 15)) and 1.49 (H(21, 21′)) — 2.15 (H(8, 18)) in the 2D NOESY spectrum define the *NXXN*-configuration of isomer **6** and the *XXXX*-configuration of isomer **7**, respectively. The assignments of the signals in the ^{13}C NMR spectra of compounds **5**—**7** made using the 2D CHCORR and 2D CHCORRLR procedures coincided with our previous assignments in the spectra of individual compounds[6] to an accuracy of 0.2 ppm. For isomers **8**—**10** with the *endo*-*endo*-configuration (· *NN* ·) of the central NB fragment the calculated CS values for the signal of the C(21) atom obtained using the known data[1] are ~50 ppm. The absence of triplet signals in this region of the ^{13}C NMR spectrum entirely rules out the presence of isomers **8**—**10** in the mixture.

Thus, the analysis of one- and two-dimensional ^{1}H and ^{13}C high-resolution NMR spectra made it possible to perform a complete assignment of all signals in the spectra of the mixture of five NBD trimers **1**, **2**, and **5**—**7** and to confirm the stereochemical identification made previously.[6,8]

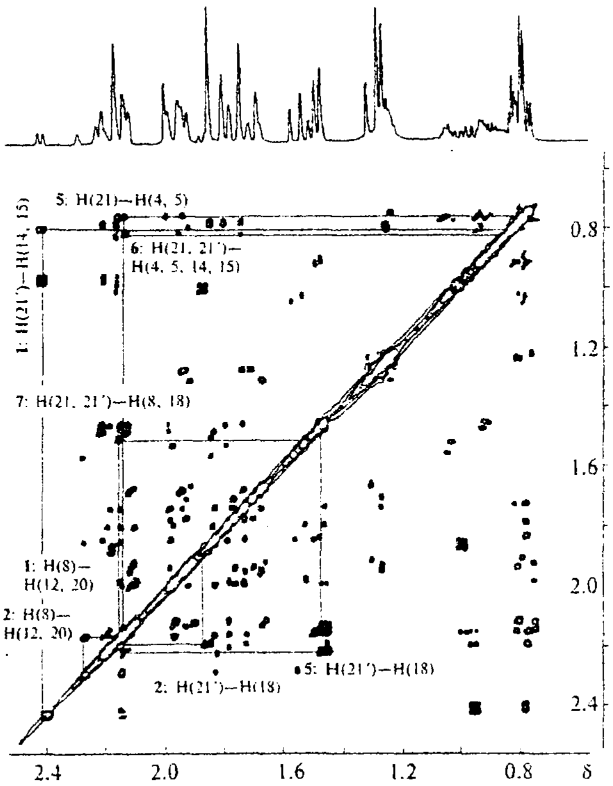

Fig. 2. NOESY spectrum of the mixture of stereoisomeric NBD trimers **1**, **2**, and **5**—**7**.

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