Brief Communications

^{13}C NMR spectra of polycyclic compounds. Bicyclo[2.2.1]heptadiene tetramers

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Comparison of experimental and calculated chemical shifts of carbon atoms in ^{13}C NMR spectra of two isomeric dodecacyclo[$14.9.1.1^{4,13}.1^{7,10}.0^{2,15}.0^{3,14}.0^{5,12}.0^{6,11}.0^{17,25}.0^{18,24}.0^{19,21}.0^{20,24}$]-octacos-8-enes, bicyclo[2.2.1]heptadiene tetramers, confirmed their *exo-trans-exo-trans-exo-endo-* and *exo-trans-exo-trans-exo-exo-*configurations.

Key words: ^{13}C NMR spectra, stereoisomers, bicyclo[2.2.1]heptadiene tetramers.

Previously we have studied the structures of bicyclo[2.2.1]heptadiene dimers and trimers and determined the stereochemistry of the obtained stereoisomers using 1D- and 2D ^{1}H and ^{13}C NMR spectroscopy.[1—4] In this work, the analysis of ^{13}C NMR spectra of two bicyclo[2.2.1]heptadiene tetramers[5] was used to confirm their structures.

Catalytic co-dimerization of norbornadiene (**1**) and quadricyclane (**2**) (Scheme 1) can result in the general case, in the formation of four stereosomers of norbornadiene tetramers (**3**—**6**).[5] Each of them belong to the point group symmetry C_s. This must lead to the pairwise coincidence, in the ^{13}C NMR spectra, of signals for the carbon atoms, which are located out of the symmetry plane. The condensation gave two isomers that differed in their spectral characteristics. Chemical shifts (CS) in the ^{13}C NMR spectra were calculated by an additive scheme using a program we had developed.[2] CS for the dimers and trimers were used as the database for the CS increments.[3,4] The calculated CS values are presented in Table 1, along with the closest experimental values.

Comparison of these data shows that the compounds obtained correspond to stereoisomers **3** and **4**. In this case, the mean difference between the calculated and experimental CS is 0.1—0.3 ppm, and the maximum deviation reaches 1.7 ppm for C-17 (C-25) in the case of isomer **3** and 0.6 ppm for C-1 (C-16) in isomer **4**. It should be noted that the intensities of the signals are consistent with the symmetry of the molecules. For the supposed structure **6**, deviations of the calculated values from the experimental ones are one order greater than those in previous cases: Δδ is 11 ppm for C-26; in addition, several deviations of 3—4 ppm are observed. The

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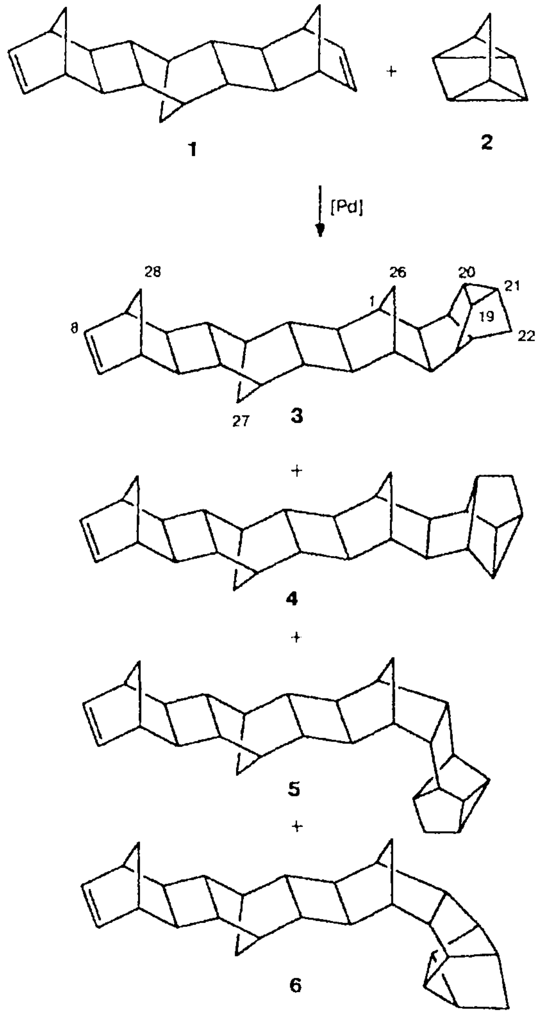
Scheme 1



calculated CS for structure **5** also have significant deviations from the experimental values: 5.5 ppm for C-26, 2—4 ppm for C-18, C-21, and C-24. Thus, stereoisomers **5** and **6** were excluded from the possible structures.

Thus, comparison of calculated and experimental CS of the carbon atoms in the ^{13}C NMR spectra has confirmed the stereochemistry of two bicyclo[2.2.1]heptadiene tetramers, *viz.*, *exo-trans-exo-trans-exo-endo-* (**3**) and *exo-trans-exo-trans-exo-exo-* dodecacyclo[$14.9.1.1^{4,13}.1^{7,10}.0^{2,15}.0^{3,14}.0^{5,12}.0^{6,11}.0^{17,25}.0^{18,24}.0^{19,21}.0^{20,24}$]octacos-8-ene (**4**).

Table 1. Calculated and experimental ^{13}C NMR chemical shifts of norbornadiene tetramers **3**—**6** (C_6D_6, δ)

Atom	**3**		**4**		**5**	**6**
	Calc.	Exp.	Calc.	Exp.	Calc.	
1, 16	40.2	40.55	44.1	43.50	43.0	43.9
2, 15	47.2	47.05	47.0	46.47	40.9	42.4
3, 14	42.5	43.33	42.5	42.72	43.2	42.5
4, 13	42.0	41.88	42.0	41.80	42.0	42.0
5, 12	41.8	41.55	41.8	41.36	41.8	41.8
6, 11	40.9	40.70	40.9	40.70	40.9	40.9
7, 10	44.4	44.21	44.4	44.21	44.4	44.4
8, 9	135.4	135.26	135.4	135.31	135.4	135.4
17, 25	49.1	47.32	50.8	50.95	49.4	47.8
18, 24	47.3	47.32	46.3	46.07	42.7	46.0
19, 20	12.7	12.92	16.7	16.81	18.5	12.7
21	17.0	17.35	11.6	11.5	13.4	13.8
22	28.1	27.90	33.5	33.57	33.7	27.4
23	43.7	43.59	39.3	39.20	38.6	50.0
26	28.9	29.20	30.5	30.24	35.7	40.2
27	29.1	29.03	29.1	29.03	29.1	29.1
28	41.8	41.67	41.8	41.67	41.8	41.8

Experimental

^{13}C NMR spectra were recorded on a Bruker AM-300 (75 MHz) spectrometer in C_6D_6 ($SiMe_4$). Resolution was 0.6 Hz. Time of delay between 45°-pulses was 3 s.

Synthesis of bicyclo[2.2.1]heptadiene tetramers was reported earlier.[5]

References

1. R. I. Khusnutdinov, V. A. Dokichev, A. A. Panasenko, L. M. Khalilov, and U. M. Dzhemilev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2492 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 2281 (Engl. Transl.)].
2. L. M. Khalilov, A. A. Gimaev, and O. V. Shitikova, *VIII Vsesoyuzn. konf. "Ispol'zovanie Vychislitel'nyh Mashin v Spektroskopii Molecul i Khimicheskikh Issledovaniyakh"* [*Use of Computers in Spectroscopy of Molecules and Chemical Investigations*], *Abstracts, Novosibirsk, 1989,* Novosibirsk, 1989, 89.
3. L. M. Khalilov, O. V. Shitikova, R. I. Khusnutdinov, Z. S. Muslimov, U. M. Dzhemilev, A. A. Panasenko, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 555 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 481 (Engl. Transl.)].
4. L. M. Khalilov, O. V. Shitikova, A. A. Gimaev, R. I. Khusnutdinov, U. M. Dzhemilev, A. A. Panasenko, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1973 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1792 (Engl. Transl.)].
5. U. M. Dzhemilev, R. I. Khusnutdinov, D. K. Galeev, A. I. Malikov, O. M. Nefedov, and Yu. V. Tomilov, *Mendeleev Commun.*, 1992, 56.

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