Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1**(3), 98–99
Mendeleev Communications

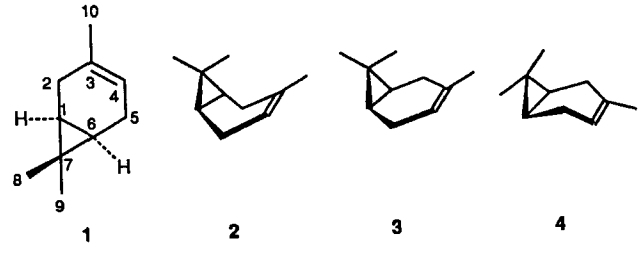
Is the Six-Membered Ring of the 3-Carene Molecule Planar?

Alexey V. Tkachev* and Alexey Yu. Denisov

Novosibirsk Institute of Organic Chemistry, Siberian Department of the Academy of Sciences of the USSR, 630090 Novosibirsk, USSR

The stable conformation of the 3-carene molecule has a practically planar six-membered ring, according to ^{1}H NMR data and molecular mechanics calculations.

The monoterpene hydrocarbon 3-carene **1** is one of the most widely occurring terpene compounds, and it is of interest as a substrate for the synthesis of a number of important products. Despite the abundance of research on its chemistry, there is a widespread mistake concerning the most stable conformation of this compound. The 3-carene molecule **1** is thought to exist in two stable conformations in solution: **2** and **4**.[1] However, in 1973, ref. 2 indicated that the six-membered ring of the 3-carene molecule should be planar or almost planar. The results of that work were disregarded and the above mistake became generally accepted. Based on the results of molecular mechanics calculations and on a comparison of the experimental values of proton–proton coupling constants with those calculated from geometric parameters and refined by molecular mechanics, this communication shows conformation **3**, in which the six-membered ring is practically planar, to be the only stable conformation of 3-carene.



Scheme 1

We have analysed in detail the ^{1}H NMR spectrum of 3-carene **1** recorded on a Bruker AM-400 instrument at an operating frequency of 400.13 MHz, and experimental values of spin–spin coupling constants $^nJ_{H-H}$ obtained by the iteration program PANIC (Table 1). These values were found to differ

Table 1 ^{1}H NMR parameters for carene **1** [a]

H Atom	δ_H	J_{H-H}/Hz (± 0.2)[b]						
		H^2_α	H^2_β	H^4	H^5_α	H^5_β	H^6	$3H^{10}$
H^1	0.711	7.8	0.5	0.0	0.0	0.0	9.1	0.0
H^2_α	2.166		18.4	2.0	2.2	2.3	0.0	1.0
H^2_β	1.801			2.0	2.3	4.5	0.0	1.0
H^4	5.232				3.6	3.6	0.6	1.4
H^5_α	2.343					19.0	7.8	2.2
H^5_β	1.948						0.5	2.2
H^6	0.610							0.0
$3H^8$	0.760							
$3H^9$	1.020							
$3H^{10}$	1.595							

[a] 1% $CDCl_3$ solution, 25 °C. [b] Sign of coupling constant not determined.

by 0.2–1.6 Hz from those published earlier.[2] Table 2 lists the calculated values of proton–proton coupling constants both for the non-planar forms **2** and **4**, and for conformation **3** with a planar six-membered ring. For the non-planar forms **2** and **4**, the proton–proton coupling constants were calculated using geometries estimated from Dreading models, and for the planar form **3**, using a molecular geometry refined by molecular mechanics.[3] The molecular mechanics calculations were carried out using the MMP2 program.[4] As shown in Table 2, the experimental data agree with the calculated data for the planar form **3** but not for conformations **2** and **4** separately or in the case of exchange between the equally adopted forms **2** and **4** (the proton–proton coupling constant values at − 80 °C in the CS_2 solution are practically the same as those given in Table 1, which suggests the same adoption of these conformations on condition that they can interconvert). Moreover, molecular mechanics calculations, with specification of the geometry of either form **2** or **4** as the starting geometry and energy minimization, leads to the same planar form **3** ($\phi_{C^1-C^2-C^3-C^4}$ = 5.8°, $\phi_{C^3-C^4-C^5-C^6}$ = − 6.5°).

Table 2 Selected proton–proton coupling constants for 3-carene **1**

H^i–H^j	J/Hz				
	Calculated[a]				Experimental
	2	**3**	**4**	**2**⇌**4** [b]	
H^1–H^2_α	1.8	6.8	9.7	5.8	7.8
H^1–H^2_β	3.3	0.3	4.1	3.7	0.5
H^6–H^5_α	1.8	6.8	9.7	5.8	7.8
H^6–H^5_β	3.3	0.3	4.1	3.7	0.5
H^2_α–H^2_β	− 13.5	− 19.2	− 13.5	− 13.5	18.4
H^5_α–H^5_β	− 13.5	− 19.2	− 13.5	− 13.5	19.0

[a] Vicinal proton–proton coupling constants were calculated using the formula $^3J = 10\cos^2\phi$;[5] the geminal proton–proton coupling constants ^2J from the value of the bond angle C—CH_2—C considering the contribution of J^π of the neighbouring π-bond.[6,7] [b] In the case of fast exchange between equally adopted conformations.

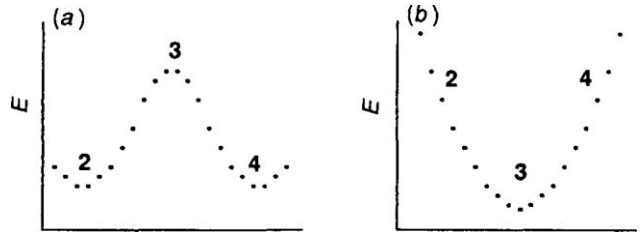


Fig. 1 (*a*) Incorrect and (*b*) correct conformational energy distributions for the three possible conformations of 3-carene

Thus there is ample reason to propose that the form of the 3-carene molecule **3** with a practically planar six-membered ring corresponds to a stable conformation, rather than the transition state of the transformation **2**⇌**4** (Fig. 1).

Received in USSR, 2nd April 1991
Received in UK, 29th May 1991; Com. 1/01710A

References

1 W. F. Erman, *Chemistry of Monoterpenes. An Encyclopaedic Handbook*, Part B, Marcel Dekker, New York, 1985, p. 870.
2. R. J. Abraham, M. A. Cooper and D. Whittaker, *Org. Magn. Reson.*, 1973, **5**, 515.
3 A. V. Tkachev, O. V. Toropov, G. E. Salnikov, Yu. V. Gatilov and I. Yu. Bagryanskaya, *Zh. Org. Khim.*, 1989, **25**, 249 (English translation in *J. Org. Chem. USSR*, 1989, **25**, 220).
4 T. Clark, *A Handbook of Computational Chemistry*, Wiley, New York, 1985.
5 R. J. Abraham and G. Gatti, *Org. Magn. Reson.*, 1970, **2**, 173.
6 R. C. Cookson, T. A. Grabb, J. J. Frankel and J. Hudes, *Tetrahedron*, Suppl., 1966, **7**, 355.
7 M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, 1963, **85**, 1899.