Carbon-13 Nuclear Magnetic Resonance Spectral Analysis of Semibullvalene and Related Substances

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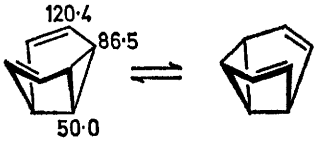
Summary The ^{13}C n.m.r. spectra of semibullvalene and a number of its annulated derivatives provide valuable information on the direction of the valence tautomeric equilibria in nondegenerate examples.

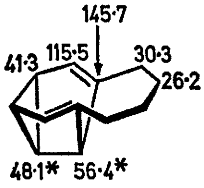
In view of the possibility of gaining valuable insight into the structure of fluxional, olefinic, and non-benzenoid aromatic hydrocarbons from ^{13}C n.m.r. spectroscopy,[1] a method of analysis sensitive to differences in bond type in carbon compounds, the recently prepared[2] polyolefins (**2**), (**3**),[3] (**4**), and (**6**) were analysed by this technique. Natural abundance ^{13}C n.m.r. spectra[4] of the four hydrocarbons and the models semibullvalene (**1**) and 1,6-methano[10]annulene (**5**) were recorded and all chemical shifts assigned, as denoted on the formulae.[5]

Semibullvalene (**1**) reveals an easily reconcilable three-line spectrum, while the annulene (**5**) exhibits a simple four-line spectrum, the distinction of whose methine signals is made tentatively by analogy with known naphthalene shifts.[6] The spectrum of hydrocarbon (**6**) displays only π-bonded carbon signals except for the two lines of the methines of the ubiquitous two-carbon bridge whose relative shift constancy facilitates their recognition among the hydrocarbons (**2**)—(**4**) and (**6**).[7] The low-intensity signal of the quaternary carbons[8] in the spectrum of (**6**) distinguishes them from methines of similar chemical shift. The 127·5 and 130·8 p.p.m. signals of (**6**) can be assigned by their similarity with the methine shifts of the annulene (**5**), while symmetry consideration leads to assignment of the remaining methine signals.

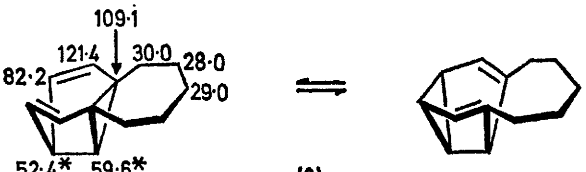
The methylenes of hydrocarbons (**2**)—(**4**) are characterized by their high-field positions and distinguished from each other on the basis of consideration of substituent effects.[9] The δ value alloted to the cyclohexenyl olefinic methines of (**4**) is derived from the methine shift of 9,10-methano-1,4,5,8,9,10-hexahydronaphthalene.[1] Finally, shift consignment of the three carbon pairs in (**2**)—(**4**) potentially involved in ring-chain tautomerism is founded on the following arguments. Hydrocarbon (**2**) reveals characteristic trisubstituted double bond signals[10,11] and a saturated methine signal whose double intensity distinguishes it from the methines of the two-carbon bridge. Both (**3**) and (**4**) possess slowly relaxing, quaternary carbons,[8] olefinic methines reminiscent of the central ones in (**1**), and olefinic methines of unusual chemical shifts.



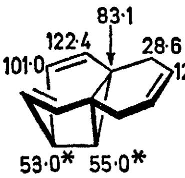
(**1**)



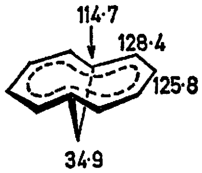
(**2**)



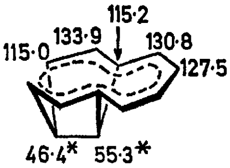
(**3**)



(**4**)



(**5**)



(**6**)

With all chemical shifts designated, it is possible to make a preliminary investigation of the tautomeric equilibrium positions of compounds (**2**)—(**4**) by comparison of the δ value of the fully olefinic methines of semibullvalene (**1**) with the shifts of the corresponding centres in the bridged analogues and by evaluation of the expected change in this value on bridging across vicinal olefinic or cyclopropanoid carbons. Since placement of a polymethylene unit onto olefinic sites would be expected to move the 120·4 p.p.m. signal of (**1**) upfield by *ca.* 5 p.p.m.[12] and corresponding substitution at the cyclopropanoid carbons would lead to an opposite shift direction also by *ca.* 5 p.p.m., hydrocarbon (**2**) appears to possess the structure indicated in its formula, triene (**4**) is made up mainly of the other tautomeric form, and (**3**) assumes an intermediary position.

The limiting structure of (**2**) is confirmed by the δ values of the remaining two sets of carbons involved in potential tautomerism. The difference of the cyclopropanoid methine shift of (**2**) and the average C n.m.r. value of a half-olefinic, half-cyclopropanoid carbon in (**1**) should be reflected in the non-protonated carbon shift of (**2**) *i.e.*, Σ 86·5 + (86·5 − 41·3) + (substituent effects[9,13]) p.p.m. The crudely calculated value of *ca.* 152 p.p.m. is indeed close to the observed shift of 145·7 p.p.m. Similar consideration of the relevant shifts of (**3**) and (**4**) confirms the tautomer dispositions of these fluxional substances indicated above.

Comparison of the two sets of 115 p.p.m. values in (**6**) with the shifts of related carbons in (**2**)—(**4**) indicate that (**6**) cannot be involved in valence tautomerism. The identity of the shifts of the quaternary carbons of (**5**) and (**6**) as well as the low-field position of the methines at 115·0 p.p.m. in (**6**) confirm this conclusion. These arguments and the aforementioned fully π-bonded nature of ten carbons of (**6**) suggest the compound to be the first neutral, homoaromatic substance.

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[1] *Cf.* H. Gunther and T. Keller, *Chem. Ber.*, 1970, **103**, 3231.

[2] L. A. Paquette, R. E. Wingard, jun., and R. K. Russell, *J. Amer. Chem. Soc.*, 1972, **94**, 4739.

[3] L. A. Paquette and R. K. Russell, unpublished observations.

[4] Noise resonance decoupled spectra of deuteriochloroform solutions were taken at 15·08 MHz on a Fourier transform spectrometer at ambient temperature. The chemical shifts are listed in p.p.m. downfield of TMS ($\delta CDCl_3 = \delta TMS + 76{\cdot}9$ p.p.m.).

[5] Starred values may be interchanged.

[6] A. J. Jones and D. M. Grant, *Chem. Comm.*, 1968, 1670.

[7] In view of the proximity of the extra ring [distinguishing these substances from (**1**)] to the central methines they are assigned the low-field position in all these compounds.[9]

[8] The signal was nearly missed at a 5 s pulse recycle rate and required a 10 s recycle time for clear observation.

[9] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984; D. K. Dalling and D. M. Grant, *ibid.*, 1972, **94**, 5318.

[10] E. Wenkert and B. L. Buckwalter, *J. Amer. Chem. Soc.*, 1972, **94**, 4367.

[11] Presumably strain causes greater shielding of the methines and deshielding of the non-protonated carbons.

[12] R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, 1963, **85**, 1300. G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, 1964, **68**, 1965.

[13] The Grant α and β effects[9] would be expected to contribute up to 20 p.p.m. downfield shift. Other difficultly calculable effects (*e.g.*, strain) are shielding by nature and thus would lower this value.