Carbon-13 Hyperfine Splittings and Geometry at the Radical Center in Bicyclo[2.2.1]hept-2-yl Radicals

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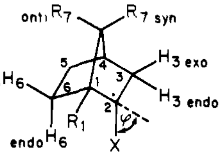
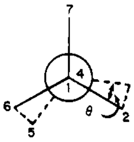
Abstract: The paramagnetic adducts between organosilicon, -germanium, or -tin centered radicals and camphor and thiocamphor give ESR spectra sufficiently intense to allow the detection of the metal satellite lines as well as those of the naturally abundant ^{13}C atoms. Although the magnitude of the hyperfine splitting from the α carbon is indicative of a certain degree of pyramidalization at the radical center, the comparison with the same splittings for noncyclic radicals bearing similar substituents suggests that the observed nonplanarity in our bicyclo[2.2.1]hept-2-yls is essentially an effect of the substituent rather than of the bond-angle straining. INDO-MO calculations have also been carried out on model systems to obtain estimates of the degree of pyramidalization in the title radicals.

The geometry at the radical-center carbon atom in bicyclo[2.2.1]hept-2-yl radicals has been the subject of debate during recent years.[1-5] Fujimoto and Fukui[6] argued that a pyramidal radical center at C_2 would be favored by the straining of the C_1-C_2-C_3 bond angle, which in norbornane is reported to be 104.3°,[7] a value much smaller than that required for sp^2 hybridization (120°). The inequivalence of the hyperfine splittings at the two β protons on C_3 observed in the ESR spectra of the majority of bicyclo[2.2.1]hept-2-yls investigated so far has been actuall taken by several authors as evidence for nonplanarity at C_2,[1-3,5] this meaning that the C_2X bond (where X is the leading atom of a substituent in position 2) is not contained in the $C_1C_2C_3$ plane. Since the larger of these two couplings could be assigned to the exo proton by studying the radical from isoborneol selectively deuterated at the 3-exo position,[3] it has been concluded that the C_2-X bond is tilted in the endo direction in agreement with the suggestions by Fukui.[6] Estimates of the degree of pyramidalization at the radical center have been made by comparing the difference $a_{3_{exo}} - a_{3_{endo}}$ with the values predicted by SCF-MO calculations carried out on model systems for different angles φ between the C_1-C_2-C_3 plane and the C_2-X bond.[2,3,5] The estimated values of φ are in the range 20-40°, φ being larger for derivatives bearing electronegative substituents, such as OH, bonded to the radical center. These caluculations were performed on the assumption that the C_1, C_2, C_3, and C_4 atoms lie in the plane bisecting the H(3-exo)-C_3-H(3-endo) bond angle, as in norbornane.

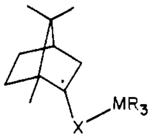


On the other hand, deviation from planarity to such an extent is not justified, in derivatives unsubstituted at the 2-position, by the experimental α-proton splittings which are consistent with a planar structure or at most with a pyramidalization at C_2 of only a few degrees. For this reason Marx and Bonazzola[4] suggested, as an alternative explanation, that the inequivalence of the two β protons on C_3 could be due to a twisting of the molecule around the C_1C_4 axis. Support to this hypothesis was provided by the observation that substituted bicyclo[2.2.1]heptanes may adapt themselves to the strain induced by certain substituents by adopting a distorted geometry which can be visualized as derived from norbornane by a "partial pseudorotation" about the C_1C_4 axis.[8] Experimental values of the dihedral angle ϑ between the $C_1C_2C_4$ and $C_1C_3C_4$ planes may be as large as 6-10°. Thus, if the presence of a substituent in norbornane produces a significant distortion of the molecular skeleton, it is conceivable that a similar effect results also by the presence of an unpaired electron. On these grounds, Marx and Bonazzola estimated that an anticlockwise rotation of C_3 of 8° in bicyclo[2.2.1]hept-2-yl (X = H) and 16° in 2-hydroxybicyclo[2.2.1]hept-2-yl (X = OH) may well account for the magnitude of the β-proton hyperfine splittings, even with the condition of planarity at C_2.



The determination of the ^{13}C coupling at C_2 would allow one to decide between the two proposed hypotheses, since $a(^{13}C)$ values smaller than ca. 40 G provide evidence for planarity or nearly so at the radical center, while larger splittings are indicative of pyramidalization.[9] However, in the bicyclo[2.2.1]hept-2-yls reported so far, the radical concentration was in no case large enough to allow the detection of the naturally abundant ^{13}C satellites, and therefore the geometry adopted by this class of radicals is still an open question.

For this reason we have examined the paramagnetic adducts resulting from the addition of group 4B organometallic radicals to camphor and thiocamphor, since similar adducts from hindered ketones or thioketones were found to give intense ESR spectra.[10] Radicals **1** and **2a-f** were in fact quite persistent and gave ESR



1a, X = O; $MR_3 = SiPh_3$
2a, X = S; $MR_3 = SiPh_3$
b, X = S; $MR_3 = SiEt_3$
c, X = S; $MR_3 = GePh_3$
d, X = S; $MR_3 = SnPh_3$
e, X = S; $MR_3 = SnMe_3$
f, X = S; $MR_3 = Sn(n\text{-}Bu)_3$

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Table I. ESR Spectral Parameters for the Spin Adducts between $R_3M\cdot$ Radicals and Camphor and Thiocamphor[a]

radical	MR_3	a^H(3-*exo*)	a^H(3-*endo*)	a^H(6-*exo*)	$a^C(^{13}C_2)$	$a^C(^{13}C_6)$	a^M	*g*
1a	$SiPh_3$[b]	29.92	17.67	7.98	70.5	*c*	6.95	2.0031
2a	$SiPh_3$[d]	31.97	22.52	8.61	48.1	19.1	9.48	2.0039
2b	$SiEt_3$	31.02	21.96	8.43	47.9	18.8	9.15	2.0040
2c	$GePh_3$	31.17	22.37	8.54	46.5	19.7	6.61	2.0038
2d	$SnPh_3$	31.17	22.20	8.50	*e*	*e*		
2e	$SnMe_3$	30.65	22.09	8.43	*e*	*e*	126.7[f] 133.5[g]	2.0035
2f	Sn(*n*-Bu)$_3$	30.37	21.86	8.26	*e*	*e*	102.5[f] 107.3[g]	2.0036

[a] Hfs constants are given in gauss, = 10^{-4} T. [b] An additional multiplet with a separation of 0.45 G is observed. [c] Not resolved. [d] An additional multiplet with a separation of 0.153 G is observed. [e] The ^{13}C satellites are hidden by the tin hyperfine structure. [f] ^{117}Sn. [g] ^{119}Sn.

spectra sufficiently intense (see Figure 1) to observe satellites by the naturally abundant ^{29}Si, ^{73}Ge, ^{117}Sn, ^{119}Sn, and, more important, ^{13}C nuclei. The measured hyperfine splitting constants are reported in Table I.

The values of ^{13}C coupling at the α carbon, i.e., 70.5 and ca. 48 G in the silyl adducts from camphor and thiocamphor, respectively, are certainly indicative of nonplanarity at C_2; however, they are not much larger than in related noncyclic radicals where no straining of the bond angles at the radical-center carbon atom is present. For example, $a(^{13}C)$ is 65.05 G in the dimethyl(hydroxymethyl) $Me_2\dot{C}OH$,[11] and 47.6 G in the di-*tert*-butyl[(tri-*n*-butylsilyl)thio]methyl $(Me_3C)_2\dot{C}SSi(n\text{-}Bu)_3$.[10] This suggests that nonplanarity at C_2 in our bicyclic radicals is mainly an effect of the substituent rather than of bond angle straining.

To have an estimate of the degree of pyramidalization the hyperfine splittings were calculated for the model SiH_3 adducts from camphor and thiocamphor with the unrestricted SCF-MO method within the INDO approximation. The carbon skeleton of the radical and the positions of the protons were assumed to be the same as in norbornane;[7] the C–O and C–S bonds were assumed to be tilted toward the endo side, and the O–Si and S–Si bonds were assumed to point in the exo direction. C–O and C–S bond distances of 1.347 and 1.784 Å and ∠COSi and ∠CSSi bond angles of 126.3 and 95.8° were used. These values are the result of a geometry optimization in the model radicals $Me_2\dot{C}OSiMe_3$ and $Me_2\dot{C}SSiMe_3$. The hyperfine splittings and the total energies computed as a function of the angle φ between the $C_1C_2C_3$ plane and the C–X bond are shown in Figures 2 and 3, respectively.

The comparison of the experimental and calculated ^{13}C hyperfine splittings provides values for the φ angle of 27.5 and 13.5° in the silyl adducts of camphor and thiocamphor, respectively. In the former radical this angle corresponds to the minimum (see Figure 3) of the potential energy curve, while in the latter one the minimum is found at a slightly large value of φ (17.5°). These calculations also reproduce reasonably well the difference between the coupling at the 3-exo and 3-endo protons and allow us to assign to C_6 the ca. 19-G splitting observed at a second carbon atom in the adducts **2a–c**, on the basis of the computed couplings at C_1, C_3, C_6, and C_7 which are ca. −6, −9, 12, and 2 G, respectively. Since a negative 19-G coupling is rather unlikely, we can in fact disregard C_1 and C_3.

On account of the reliability of these values, the calculations were repeated for the 2-camphyl radical (X = H), and the results are shown in Figures 2 and 3. Also in this case the INDO results favor a slightly pyramidal configuration at C_2, a very shallow minimum being found at $\varphi = 13°$ [$E(0) - E(13) = 0.14$ kcal/mol]. However, the energy profile is so flat even for H_2 tilted toward the exo direction [$E(-15) - E(0) = 0.23$ kcal/mol] that the average value of the out-of-plane angle φ should not exceed 4 or 5°.

It is worth pointing out that even in the planar configuration at C_2 of the three model radicals examined here, INDO calculations provide different values for the 3-exo and 3-endo proton couplings. This effect can be ascribed, by analogy with the consideration by Fukui et al.,[12] to a distortion of the $2p_z$ orbital centered on C_2 due to the interaction with C_1–C_6, C_1–C_7, and O–M

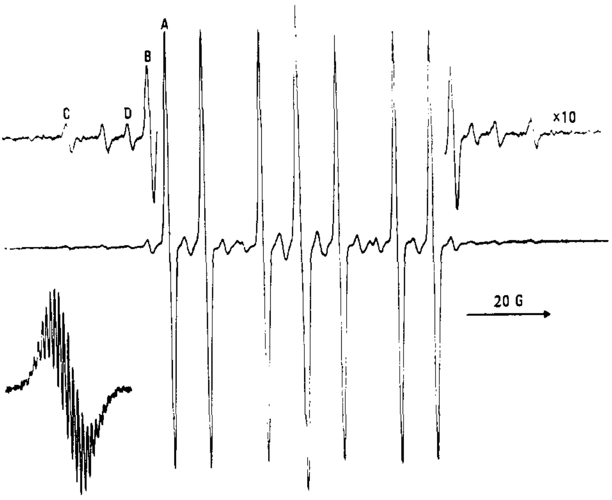

Figure 1. Room temperature ESR spectrum of radical **2a**. Lines B, C, and D of the spectrum recorded with a higher gain are the ^{29}Si, $^{13}C_2$, and $^{13}C_6$ satellites of the first line A of the main spectrum, an expansion of which is shown in the lower left side of the picture.

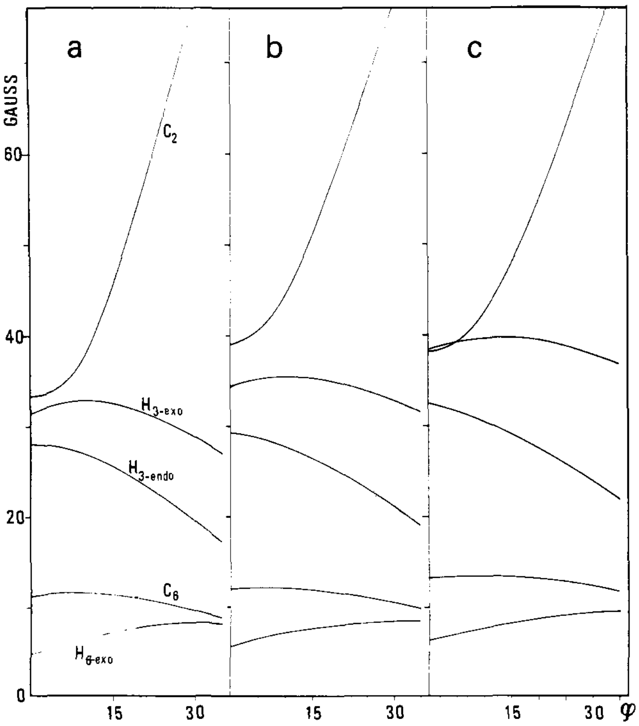

Figure 2. INDO computed dependence of some relevant hyperfine splitting constants on the angle φ between the $C_1C_2C_3$ plane and the C_2–X bond in the silyl adducts of (a) camphor and (b) thiocamphor and (c) in the camphyl radical.

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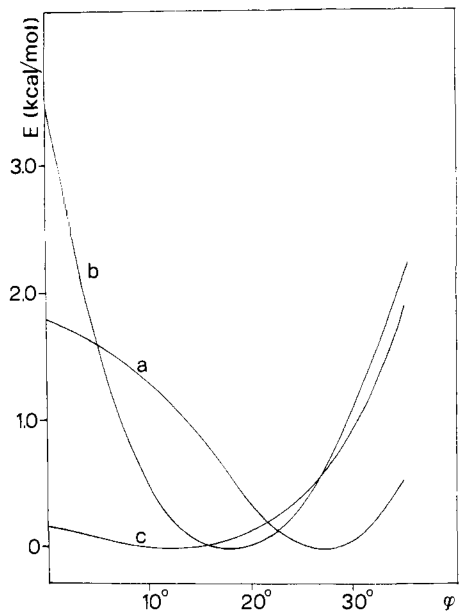

Figure 3. INDO potential energies computed as a function of the angle φ between the $C_1C_2C_3$ plane and the C_2–X bond in the silyl adducts of (a) camphor and (b) thiocamphor and (c) in the camphyl radical.

or S–M bonds which are not symmetrical with respect to the $C_1C_2C_3C_4$ plane. In fact if the C_2–X bond is tilted toward the exo side, the a^H(3-exo) − a^H(3-endo) difference tends to vanish.

In conclusion, the experimental and computed results reported here have shown various interesting points that can be summarized as follows. (i) The radical-center carbon atom in bicyclo[2.2.1]hept-2-yls and related radicals shows only a slight tendency to adopt a pyramidal geometry as the result of the straining of the $C_1C_2C_3$ bond angle. (ii) The degree of pyramidalization, which is expected to be quite small for X = H, can be considerably larger when electronegative substituents X, having a π-type lone pair, are attached to C_2. First-row heteroatoms cause a greater pyramidalization than second-row heteroatoms, in agreement with theoretical predictions.[13] (iii) Estimates of the tilt angle based on the difference between the 3-exo and 3-endo proton couplings may be misleading, since these splittings are predicted to be inequivalent even for a planar configuration at C_2. Moreover, distortions of the carbon skeleton resulting in a twisting of the molecule around the C_1C_4 axis may further increase this inequivalence.[4]

Experimental Section

The transient metal-centered radicals were generated within the cavity of the ESR spectrometer by room temperature photolysis, with a high pressure mercury lamp, of degassed solutions of the carbonylic or thiocarbonylic substrate in *tert*-butylbenzene containing the appropriate triaryl or trialkyl metal hydride and di-*tert*-butyl peroxide.[14] With camphor only the silyl adduct could be observed in these conditions. While thiocamphor was prepared according to well-established methods, all other chemicals were commercially available and were used without further purification.

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Threshold Intensities and Kinetics of Sonoreaction of Thymine in Aqueous Solutions at Low Ultrasonic Intensities

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Abstract: In this study, the threshold intensities and kinetics of sonoreaction of thymine in aqueous solutions are investigated under different experimental conditions. The results show that in the limiting case of zero aeration rate the threshold for thymine reaction is 1.7 W/cm^2. The experiments were carried out under a controlled and well-defined acoustic field and the influence of various important factors (spatial average acoustic intensity, bubbling rate, solution temperature kinetics) has been investigated. Tentative theories of cavitation and the accompanying chemical processes are proposed on the basis of experimental results. At relatively higher acoustic intensities (>3 W/cm^2) the cavitation chemistry of thymine is significantly reduced. This has been attributed largely to the change in the number of cavitating bubbles due to an increasing degree of coalescence. The results also suggest that the sonoreaction may take place in the bubble–liquid interphase and the reaction kinetics change with the solution temperature. This is due to converse changes in cavitation intensity and thymine diffusion as the solution temperature is altered.

Nucleic acid components, under a variety of experimental conditions, are known to undergo sonoreaction in an ultrasonic field.[1-5] These studies largely deal with the production, isolation, and identification of sonoproducts. In order to understand ultrasonic toxicity at a molecular level, it is necessary to investigate the reaction kinetics, the threshold intensities for the reactions of nucleic acid components, and how the threshold intensities change with cavitation conditions, viz., bubbling activity, solution temperature, etc.

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