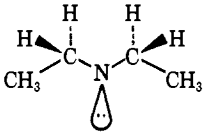
magnitude of the β-hydrogen coupling constant with the angle θ between the C–H bond and the axis of the p orbital containing the unpaired electron it is possible to estimate θ for the time-averaged equilibrium conformations of diethylamino and diisopropylamino radicals as 35 and 60°, respectively. It is obvious from an examination of molecular models that the rather decided conformational preferences in these radicals arise from steric interactions of the alkyl groups. These effects are minimized in diethylamino radical when the C–C bond of each ethyl group lies approximately in the nodal plane of the nitrogen p orbital (**2**) and in diisopropylamino radical when the C–H bond approaches to within about 35° of the nodal plane (**3**).



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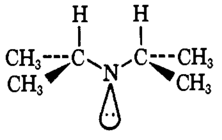

3

The spectrum of the latter species was observed to be almost invariant over a 150° temperature range (−120 to +30°). Although the fortuitous near equivalence of the nitrogen and hydrogen hyperfine coupling constants complicated by the hyperfine interaction of the twelve γ-hydrogens precluded an exact assessment of the β-hyperfine coupling constant, it appears that there is a change of less than 0.5 G over the temperature range investigated.

No evidence was observed under our photolytic conditions for any transformations involving hydrogen migration in these dialkylamino free radicals.[14,15]

We are presently investigating a wide variety of neutral amino free radicals in solution.

Acknowledgments. We wish to acknowledge Dr. K. F. Purcell of Kansas State University for assistance with the INDO calculations and Dr. P. J. Krusic of E. I. du Pont de Nemours and Co., Central Research Department, for helpful suggestions on assembling the irradiation apparatus.

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Received June 8, 1970

Nuclear Magnetic Resonance Spectrum of Oriented Bullvalene

Sir:

It is well known that valence-bond isomerization can have a striking effect on the isotropic nmr spectra of fluxional molecules;[1] line shapes and splittings depend on the rate of the isomerization *vis-à-vis* the difference in resonant frequencies of individual structures. Similarly, when a static (*i.e.*, nonisomerizing) molecule is partially oriented in the anisotropic environment of a liquid crystal solvent, the spectral characteristics are influenced by the rate of exchange among ordered and disordered sites relative to the difference in resonant frequencies of molecules in these sites.[2] If the two situations are combined, and a fluxional molecule is dissolved in a liquid crystal solvent, all three processes are competitive, and a fourth, the rate of reorientation of the solute molecule in an ordered site, may enter if isomerization disturbs the local ordering. A dramatic example is provided by a nematic solution of bullvalene (tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene).[1] The purpose of this communication is to report the nmr spectrum of oriented bullvalene, and the ordering parameter[3] of the static molecule.

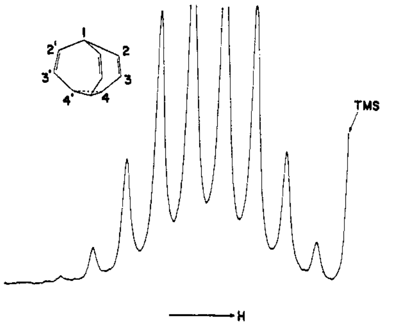

Figure 1. ^{1}H nmr spectrum of bullvalene oriented in a nematic liquid crystal solvent at 130°, read out after 60 runs on a C-1024 computer of average transients. The spectrum was read out at high gain to show up the downfield line; as a result, the two most intense lines are off the chart paper.

A 30 mol % solution of bullvalene in *p*-bis(heptyloxybenzoyloxy)benzene containing a few drops of TMS was degassed and sealed; the nematic range of this solution is 112–174°. The ^{1}H nmr spectrum at 130°, shown in Figure 1, is a symmetrical ten-line multiplet with 54-Hz spacing. The width of the lines (20 Hz) is about five times that normally observed in nematic solutions, and intensity measurements are unreliable because of the overlap. Nevertheless, the spectrum is unmistakably characteristic of an oriented system of ten magnetically equivalent spin-$^1/_2$ nuclei.[4] The separation between lines is three times the coupling constant, and intensities are in the ratio of the binomial coefficients of order ten.

The following mechanism is proposed to explain how the magnetic equivalence arises. Bullvalene orients in a configuration of minimum energy dictated by its shape and by dispersion forces.[5] The lifetime of a valence isomer at 130° is 10^{-6} sec,[6] and the exchange rate among sites ($>10^{7}$ sec^{-1})[2,7] ensures that the molecule will not isomerize at every site. Therefore, bullvalene orients like a static molecule between isomerizations; however, when a rearrangement does occur, the molecule is forced into an energetically unfavorable configuration and must reorient. A rough estimate of the reorientation rate is 10^{10} sec^{-1}; this was obtained by as-

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suming that bullvalene is a Stokes–Einstein sphere[8] of 3-Å radius[9] embedded in a continuous medium with a viscosity of 0.05 P.[10] Clearly the molecule can reorient before it leaves the site. Since eight of the ten protons change environment with each rearrangement,[6] all the protons will sample all molecular positions frequently in the time scale of the experiment ($\sim 2 \times 10^{-3}$ sec). An equivalent picture *from the spectroscopic point of view* is that bullvalene remains in a single orientation while the proton spins are permuted rapidly over the molecule. The result of this scrambling is a single H–H coupling which is a statistically weighted average of the 12 independent couplings in the static molecule

$$\bar{B} = \frac{1}{15}\left[\sum_{k=1}^{3}\sum_{l>k}^{4} B_{kl} + \sum_{m=2}^{4}\sum_{n=2'}^{4'} B_{mn}\right] \qquad (1)$$

where

$$B_{ij} = -3\gamma_H{}^2\hbar(3\cos^2\beta_{ij} - 1)S/4\pi r_{ij}{}^3$$

γ_H is the proton gyromagnetic ratio, r_{ij} is the distance between nuclei i and j, and β_{ij} is the angle between r_{ij} and the threefold molecular symmetry axis. S is the degree of orientation of the *static* molecule.[3] The nuclear indices in eq 1 are taken from the structure shown in Figure 1. In order to obtain S from the observed splitting (*i.e.*, $3\bar{B}$), it is necessary to assume a molecular geometry. The electron[11] and X-ray diffraction results for bullvalene are in good agreement; this indicates that the molecule is undistorted by solid-state forces. Thus, it has been assumed that bullvalene retains the crystalline molecular geometry in the "loose" nematic lattice. Using fractional coordinates from the X-ray data,[9] r_{ij} and β_{ij} have been calculated for all proton pairs. A value of 0.054 is then obtained for $|S|$ from the measured splitting. On the basis of shape alone, this is a surprisingly large value,[12] since the gross-shape anisotropy in bullvalene is small.[9] Perhaps dispersion forces play a large role, since another globular solute (CH_3CCl_3) does not show an unusually high degree of orientation in this solvent. The line widths show that the rearrangement rate is not sufficiently fast to average the dipolar interactions completely and bring the spectrum to the fast exchange limit.[13] When the temperature is raised, the lines sharpen, indicating that averaging of the coupling constants is becoming more effective.

Two limiting cases are evident for the nmr spectrum of an oriented isomerizing molecule: (1) if the rate of either thermal reorientation or of site exchange is faster than the rate of isomerization, the molecule will remain oriented, and (2) only if the isomerization is faster than both of these processes will the molecule become "unoriented," and show an isotropic spectrum. Clearly, the spectrum of bullvalene reported here belongs in the first category. It seems unlikely that a stable system can be found in which the molecular reorganization rate is sufficiently greater than thermal reorientation frequencies to meet the second requirement.

Acknowledgments. The author acknowledges with pleasure stimulating discussions with Dr. Earl B. Whipple of the Union Carbide Research Institute. Professor W. von E. Doering and Dr. M. Siskin kindly provided a bullvalene sample. John V. Powers assisted in preparing samples and obtaining spectra.

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Received December 18, 1969

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Spin Decoupling of Cobalt-59 in Proton Magnetic Resonance Studies of Cobalt(III) Complexes

Sir:

The conformations of coordinated ligands have been a subject of considerable interest to coordination chemists for many years.[1–5] Proton magnetic resonance (pmr) has made it possible in certain cases to determine the conformations of ligands,[6–8] primarily through the Karplus relationship of vicinal proton coupling constants to the dihedral angle.[9] Determination of the vicinal constants, however is possible only for pmr spectra which are sufficiently well resolved to permit accurate analysis.

Some of the best known coordination compounds, the cobalt(III) trisdiamines, have consistently exhibited pmr spectra of such low resolution as to render accurate analysis impossible.[10–15] Various authors have attributed this lack of resolution to intermediate inversion rates of the puckered five-membered chelate rings,[12] to a degree of residual paramagnetism, and to spin coupling of protons to long-lived nuclear spin states of cobalt-59 ($I = {}^7/_2$, 100% abundant).[10] Here we present the first experimental proof that the latter explanation is correct, as shown by the enhanced resolution produced by spin decoupling of cobalt-59.

Figure 1A shows the $-CH_2-CH_2-$ portion of the 100-MHz spectrum of $Co(en)_3{}^{3+}$ in aqueous solution at 36°. The half-width of the broad peak centered at 2.84 ppm *vs.* DSS is $\sim$23 Hz. Figure 1B shows the spectrum of $Co(en)_3{}^{3+}$ after N-deuteration (standing for several minutes in neutral 99.5% D_2O). The half-width of the peak has now decreased to $\sim$18 Hz because of the removal of H–N–C–H spin couplings.

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