

complex tensor having elements α_{ij} where $i, j = \pm 1$ and 0 , and the new coordinates are obtained from Cartesian coordinates according to the definition $\pm 1 = 2^{-1/2}(\mp ix + y)$, $0 = iz$. The new tensor has the form

$$\begin{array}{ccc} \alpha_{11} & \alpha_{1-1} & \alpha_{10} \\ \alpha_{-11} & \alpha_{-1-1} & \alpha_{-10} \\ \alpha_{01} & \alpha_{0-1} & \alpha_{00} \end{array} \quad (1)$$

and it is straightforward to express any Cartesian tensor in this notation by means of a unitary transformation. The advantage of using the complex tensor is evident since ± 1 components correspond to left and right circularly polarized light. It is straightforward to show, in the case of CCl_4 for example, that the totally symmetric mode will retain the sign of polarization of the incident radiation since only the diagonal elements of l are nonzero. This will be a feature of the a_1 symmetry vibrational modes of molecules belonging to the majority of the symmetry groups and may therefore be used to identify such modes. For nontotally symmetric modes it is generally the case that the off-diagonal elements α_{1-1} , α_{-11} give the major contribution and thus the sign of circular polarization is reversed (*i.e.*, the mode acts as a half-wave plate⁸). Again this rule applies to the nontotally symmetric vibrations of molecules belonging to the majority of the point groups. Figures 1-4 illustrate how the a_1 modes may be identified immediately from the circular polarization for the range of molecules in this study. In CCl_4 (Figure 1) vibrational modes ν_2 and ν_4 have symmetry t_2 and e , respectively, and these reverse the sign of circular polarization. ν_1 on the other hand has a a_1 symmetry and consequently has the same sign circular polarization as the laser radiation. This pattern is repeated for the anti-Stokes lines. Chloroform, of lower symmetry, consequently has more a_1 modes than CCl_4 and from Figure 2 it is clear that ν_1 , ν_2 , and ν_3 have a_1 symmetry and the remainder are nontotally symmetric. The spectrum of benzene exhibits two a_1 modes, ν_1 and ν_2 , and a number of modes of e_{2g} symmetry including a combination band. These latter all reverse the sign of polarization. Finally, the linear CS_2 molecule shows a strong ν_1 of a_1 symmetry, the remaining structure arising from hot bands and combinations.

These results indicate clearly the power of this technique as a diagnostic tool in structural analysis since the totally symmetric vibrations may be identified immediately. This rule may not apply to molecules of very low symmetry, C_1 , C_2 , C_i or C_s for instance, in which the α_{xy}, α_{yz} , polarizability components may transform in the same way as α_{xx}, α_{yy} . This restriction also applies to conventional measurements of depolarization ratios. The circular polarization ratios obtained in our experiment are determined by squares of scattering tensor elements for the vibration concerned (or sums of these for degenerate vibrations) averaged over all molecular orientations and thus we obtain information on the $\alpha_{\rho\sigma}$ polarizability components where $\rho, \sigma = x$ or y . Linear differential intensities measured perpendicular to the exciting beam give access to the components in which $\alpha_{\rho, \sigma}$ contains the z coordinate. Together with the tensor components from circularly polarized scattering, these provide data which characterizes the complete

(8) We are indebted to Professor S. F. Mason for this analogy.

Raman spectrum, and results of these more extensive studies will shortly be reported.

Acknowledgments. We thank the S. R. C. for equipment and for research studentships (R. C., S. R. J., and R. A. S.). We also thank Professor S. F. Mason and Mr. P. A. Madden for stimulating discussions.

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Received March 19, 1974

Direct Observation of the Optical Absorption Spectra of Reactive Free Radicals at Room Temperature

Sir:

The preparation of reactive free radicals in concentrations high enough for their direct observation by optical spectroscopy has until recently depended on the use of special experimental techniques such as low temperature matrix isolation^{1,2} and flash photolysis.³ Experiments of this type usually rely on rather elaborate instrumentation for their execution and do not in most cases lead to positive assignments of the species responsible for the observed spectra. In this communication, we wish to report the development of a new method for obtaining the optical absorption and emission spectra of free radicals which not only overcomes the disadvantages of previous techniques but also permits the observation of their spectra at relatively high temperatures and under steady-state conditions.

Our approach makes use of the fact that high concentrations of free radicals can be produced by X-ray and/or uv irradiation of suitable precursors in an adamantane matrix.⁴ Thus, for example, X-irradiation of carefully purified adamantane containing a small amount of 2-methylpentane yields the 1,1-dimethylbutyl radical whose epr spectrum shows six equivalent β -protons at 23.4 G and a temperature-dependent β -methylene proton hfs of 14.9 G at 293°K.⁵ If two pressed disks of adamantane (10 mm o.d., ~1 mm thick) containing the parent hydrocarbon are placed in the sample and reference beams of a Cary 14 spectrophotometer, no absorption is observed down to 200 nm unless the disk in the sample beam has been previously X-irradiated. In that event, one observes a strong absorption feature at 218 nm which decays with a lifetime (1/e) of ~0.5 hr at room temperature. Furthermore, it is found that the lines in the epr spectrum of this radical in the *same sample* decay with the *same lifetime* at this temperature. Thus, the band at 218 nm can be assigned unequivocally to the lowest energy electronic transition of 1,1-dimethylbutyl which involves the promotion of the unpaired electron from the nonbonding orbital of π character to the lowest σ^* orbital of the radical.

As further examples of the application of this tech-

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nique, we show in Figure 1 the room temperature optical absorption spectra of the prototype hydrocarbon free radicals cyclohexenyl, cyclohexadienyl, and benzyl in the near-uv region. The cyclohexenyl radical (A) is produced by X-irradiation of cyclohexene in adamantane *via* a hydrogen atom removal process. It has epr parameters typical of an allylic system with two pairs of inequivalent β protons ($a_{1,3}^H = 14.6$, $a_2^H = 3.4$, $a_{4,6}^H = 8.4$, and $a_{4,6}^{H'} = 26.0$ G).⁵ The radical exhibits two diffuse bands at 249 and 267 nm in its optical absorption spectrum, and both of these decay with the same lifetime as the epr spectrum (0.83 hr at 298°K). Similar results have been obtained for several other cycloalkenyl radicals including cyclopentenyl, cycloheptenyl, and cyclooctenyl. In addition, the cyclooctenyl radical also shows two weak bands at 406 and 422 nm.

The cyclohexadienyl radical (B) is produced by X-irradiation of adamantane containing benzene *via* a hydrogen atom addition process and has a well-characterized epr spectrum.^{6,7} It exhibits a structured absorption spectrum in the near-uv region with the strongest features at 308 and 314 nm, and a relatively weak spectrum in the *visible* region with bands at 512 and 554 nm (not shown in Figure 1). Both the epr and optical spectra of this radical decay with a lifetime of 7.3 hr in this matrix at 298°K. The 1-methylcyclohexadienyl radical, which is produced on X-irradiation of toluene in adamantane providing care is taken to exclude O₂ from the sample,⁷ has an absorption spectrum which is essentially identical with that of cyclohexadienyl itself.

On the other hand, specific inclusion of O₂ in a sample of toluene in adamantane⁷ leads on X-irradiation to the formation of the benzyl radical as verified by its epr spectrum.^{8,9} This radical has a highly structured absorption spectrum in the near-uv region (C), with strong features at 231, 259, 294, 304, and 316 nm, and a shoulder at 324 nm which becomes weaker on lowering the temperature to $\sim 100^\circ\text{K}$ and is probably a hot band.¹⁰ No absorption has been observed at longer wavelengths in the case of benzyl. However, excitation of this radical at either 259 or 316 nm produces strong emission in the visible region in samples held at 273°K or below. Dispersion of this emission with a 0.25 m monochromator results in the well-resolved spectrum shown in Figure 1D which has an apparent (0,0) band at 461.2 nm.¹¹

Table I summarizes the results of these experiments together with assignments of the observed bands based on the restricted SCF calculations of Longuet-Higgins, Pople, and others.^{12,13} Of particular interest are the assignments for cycloalkenyl radicals. Theory predicts that the lowest energy transitions in allyl should lie at 234, 275, and 452 nm, and we observe bands at 249, 267, and 422 nm. The assignment of the band at 267 nm in the spectrum of the cyclohexenyl radical to the *spin-forbidden* ${}^4B_1' \leftarrow {}^2A_2$ transition is based primarily on the agreement between theory and experiment and

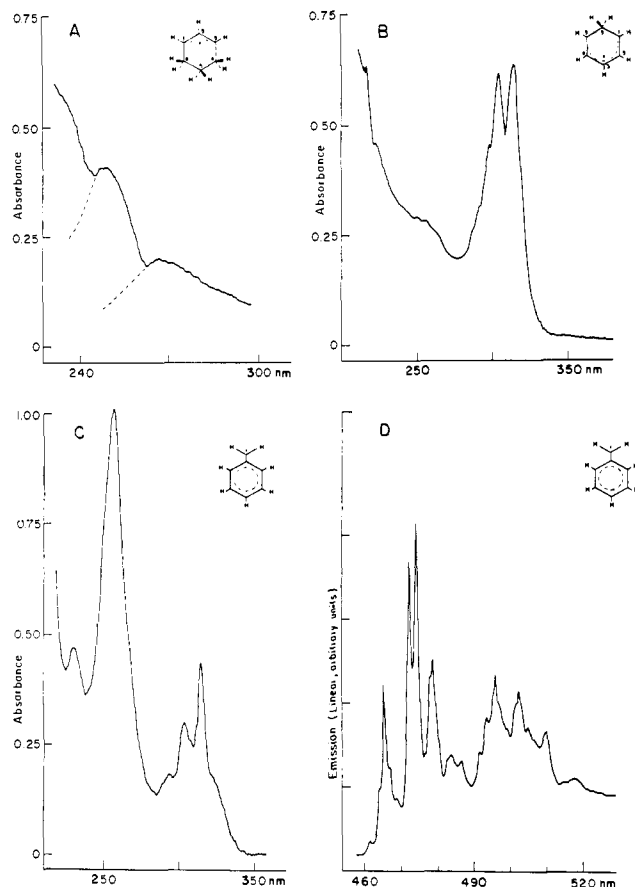


Figure 1. Optical absorption and emission spectra of free radicals in adamantane: A, cyclohexenyl radical, absorption, 298°K; B, cyclohexadienyl radical, absorption, 298°K; C, benzyl radical, absorption, 298°K; D, benzyl radical, emission, $\sim 100^\circ\text{K}$. The cyclohexadienyl radical also shows weak absorption bands in the visible region (see text).

Table I. Electronic Spectra of Free Radicals in Adamantane

Radical	Observed λ , nm	Assignment	Predicted λ , nm
1,1-Dimethylbutyl abs, 298°K	218	${}^2A_1' \leftarrow {}^2A_2'$ (D_{3h})	
Cyclohexenyl ^d abs, 298°K	249	${}^2B_1' \leftarrow {}^2A_2$ (C_{2v})	234 ^b
	267	${}^4B_1' \leftarrow {}^2A_2$	275 ^b
	422 ^c	${}^2B_1 \leftarrow {}^2A_2$	452 ^b
Cyclohexadienyl abs, 298°K	314	${}^2A_2' \leftarrow {}^2B_2$ (C_{2v})	314 ^d
	554	${}^2A_2 \leftarrow {}^2B_2$	611 ^d
Benzyl abs, 298°K	231	Rydberg	
	259	${}^2B_2' \leftarrow {}^2B_2$ (C_{2v})	199 ^b
	316	${}^2A_2' \leftarrow {}^2B_2$	297 ^b
	em, 100°K	${}^2A_2 \leftarrow {}^2B_2$	358 ^b

^a Assignments and predicted wavelengths shown are those for allyl radical. ^b H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. (London)*, **68**, 591, 1955. ^c Observed in the absorption spectrum of cyclooctenyl radical. ^d T. Shida and I. Hanazaki, *Bull. Chem. Soc. Jap.*, **43**, 646 (1970).

must be considered tentative. However, an enhancement of other multiplicity-forbidden transitions has also been observed in the absorption spectra of spin-paired systems (e.g., benzene) in adamantane.⁵ The theoretical predictions for the remaining radicals in Table I are in somewhat poorer agreement with experiment.

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(12) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. (London)*, **68**, 591 (1955).

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An examination of the literature reveals that many of the spectra described above have been previously observed by more sophisticated techniques.¹⁴ However, it is apparent that the use of the present technique offers distinct advantages for optical studies of free radicals because they are present in a host medium of high optical transparency in the uv and visible regions and can be *positively* identified by epr spectroscopy. Preliminary experiments indicate that most of the radicals which have been studied by epr using this method^{4,5,7,9,15} also exhibit strong optical spectra. These results will be described in subsequent publications from these laboratories.

Acknowledgments. Research at the University of Pittsburgh was supported in part by AEC Contract No. AT-(11-1)-3435 and by the National Science Foundation (GU-3184) and the Merck Foundation, while that at the University of Connecticut was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation.

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(15) For further examples, see D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Amer. Chem. Soc.*, **93**, 4145 (1971); D. E. Wood, C. A. Wood, and W. A. Lathan, *ibid.*, **94**, 9278 (1972); L. F. Williams, M. B. Yim, and D. E. Wood, *ibid.*, **95**, 6475 (1973); D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *ibid.*, **95**, 7978 (1973).

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Received May 9, 1974

Effect of Phase Transitions on Carbon-13 Nuclear Magnetic Resonance Spectra in *p*-Azoxydianisole, a Nematic Liquid Crystal

Sir:

Liquid crystals are comprised of long, rod-like molecules.¹ At high temperatures, they form normal liquid phases in which the molecules tumble isotropically. As the temperature is lowered, a transition occurs into a liquid crystal phase characterized by long range orientational order of the molecules. The study of these phases is of extreme interest because of their importance in several areas, including their role as model systems for biological membranes, the study of phase transitions and critical phenomena, their use as orienting solvents, etc. In this regard, nuclear magnetic resonance (nmr) has formed a valuable tool.² However, the use of nmr has been restricted

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by the near impossibility of obtaining tractable high resolution spectra of the liquid crystal molecules. This is because the magnetic dipole-dipole couplings between nuclear spins are not averaged to zero as in liquids, and the abundant protons produce a large number of overlapping lines rendering the spectra broad and intractable except in special cases such as partially deuterated materials.^{3,4} The development of techniques to obtain routinely simple, high resolution nmr spectra would clearly be quite valuable. An especially appealing possibility is ¹³C nmr, since: (a) if the ¹H spins are decoupled, the spectra should be simple and tractable due to the absence of ¹³C-¹³C couplings, (b) the chemical shielding anisotropy for ¹³C is large, thus making the nmr sensitive to orientational effects and molecular ordering, (c) spin relaxation of ¹³C is dominated primarily by intramolecular magnetic couplings. The only problems with this approach have been the traditional ones of sensitivity and resolution and the requirements of high power spin decoupling.

We have overcome the requisite technical problems and recently reported the observation of high resolution ¹³C nmr spectra in the nematic phase of *p*-methoxybenzylidene-*p*'-*n*-butylaniline (MBBA),⁵ exhibiting the effects of phase transitions, molecular ordering, conformation, and motion. This has opened the way for the application of nmr to detailed microscopic studies of structure and dynamics in liquid crystals. In this communication, we report preliminary results of work on *p*-azoxydianisole (PAA), one of the simplest compounds exhibiting a nematic phase. Figure 1 shows ¹³C nmr spectra obtained in the isotropic, nematic, and solid phases of PAA. In the isotropic phase, the chemical shifts, σ_i , are given by

$$\sigma_i = \frac{1}{3} Tr\delta \quad (1)$$

where δ are the chemical shielding tensors. In the nematic phase, rapid rotation about the long molecular axis yields an averaged tensor $\bar{\delta}$ with elements $\bar{\sigma}_{||}$ and $\bar{\sigma}_{\perp}$ along and perpendicular to the long axis and the shifts, σ , are given by

$$\sigma = \sigma_i + \frac{2}{3} S(\bar{\sigma}_{||} - \bar{\sigma}_{\perp}) \quad (2)$$

where S is the order parameter⁶

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (3)$$

and θ is the angle between the long molecular axis and the external magnetic field.

For aromatic nuclei, the general features of δ have been characterized in single-crystal studies.⁷ The

view of the Structure and Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971; (d) S. Meiboom and L. C. Snyder, *Accounts Chem. Res.*, **4**, 81 (1971).

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