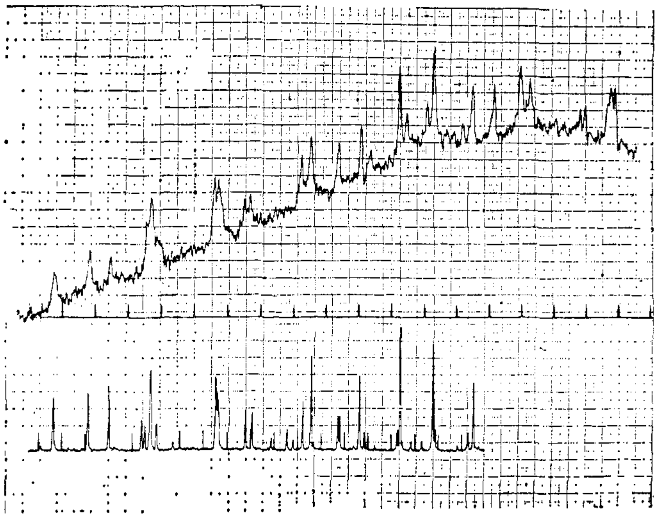

Figure 2. The top trace is the nmr spectrum at 40° of a mixture of 0.655 g of cholesteryl chloride, 0.344 g of cholesteryl myristate, and 0.01 g of benzene. The sharp lines are typical of the benzene spectrum in a nematic solvent. The very broad background resonance is due to the solvent. For comparison, the bottom trace gives a benzene spectrum in nematic hexyloxyazoxybenzene at 90°. Both traces cover a spectrum width of about 2 kHz. The center of the symmetrical benzene spectrum is midway between the two strongest lines; a number of lines at the high-field end of the spectrum are not reproduced. Frequency markers are 106 Hz apart; for the top spectrum they are given on the separate center trace, while for the bottom spectrum they are the sharp peaks superposed on the spectrum.

phase spectrum as shown in Figure 2.[5a] The alignment of the benzene is similar to that obtained in nematic *p,p'*-di-*n*-hexyloxyazoxybenzene. By proper choice of cholesteryl esters it is possible to obtain nematic phases from 23 to 130°. It is clearly possible to produce a nematic phase from a mixture of cholesterol derivatives, each of which alone would give a cholesteric mesophase. The cholesterol derivatives are colorless and lack the polarizable aromatic and conjugated systems which occur in most compounds which form a nematic phase. The mixtures are a possibly useful new solvent for studies of the polarization of optical transitions in oriented solute molecules.

In conclusion, it seems most appropriate to paraphrase Friedel's remarks: The nematic phase is but a special case of the cholesteric; it is one in which the pitch of the helical structure is infinite.

(5a) NOTE ADDED IN PROOF. The relative line positions and intensities in the top spectrum of Figure 2 differ to some degree from those in the bottom spectrum. Note for instance that the two lines nearest the center of the spectrum are stronger and farther apart in the top spectrum than in the bottom spectrum. We have recently found that this is due to the fact that in the first case the preferential alignment of the benzene is with its plane perpendicular to the magnetic field, while it is parallel to the magnetic field in the second case.

(6) On leave of absence from the Max-Planck Institut für Spektroskopie, Göttingen, Germany.

Erich Sackmann,[6] Saul Meiboom, Lawrence C. Snyder
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

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Thermal Instability of 1- and 2-Norbornyl and of 1-Bicyclo[2.2.2]octyl Radicals in a Mass Spectrometer

Sir:

In view of continuing interest in the energies of bridgehead species[1] (cations,[2] anions, and free radicals[3]), an attempt has been made to measure the ionization potentials of 1- and 2-norbornyl and 1-bicyclo[2.2.2]octyl free radicals in a mass spectrometer. For this purpose samples of 1-norbornylcarbinol,[4] 2-norbornylcarbinol,[5] and 1-bicyclo[2.2.2]octylcarbinol[6] were prepared and converted[7] to the corresponding nitrite esters (RCH_2ONO). These were subjected to thermal decomposition at pressures of $\sim 10^{-3}$ torr and temperatures of 400–450° in a fused-silica capillary furnace coupled to the ionization chamber of a mass spectrometer.[8] The decomposition of nitrites is known to proceed by the reactions[8]

$$RCH_2ONO \xrightarrow{E \sim 36\ \text{kcal}} RCH_2O\cdot + NO$$

$$RCH_2O\cdot \xrightarrow{E \sim 12\ \text{kcal}} R\cdot + CH_2O$$

In spite of the relatively low temperature and short contact time (~1 msec) employed, the radicals investigated were found to decompose further or to rearrange to more stable monocyclic radicals. This isomerization prevented the determination of the ionization potential of the parent species.

The thermal decomposition of 2-norbornylmethyl nitrite gave a small yield of C_7H_{11} radicals, as detected by an increase in the mass 95 peak when using a low-energy ionizing electron beam. The observed ionization potential was 8.1 v. Titration of this radical with phenyl radicals, produced simultaneously by thermal decomposition of *t*-butyl perbenzoate, yielded a coupling product whose mass spectrum was similar to, but not identical with, that of 2-*exo*-phenylnorbornane.[9] The main mode of dissociation of the C_7H_{11} radical was the loss of a hydrogen atom to give C_7H_{10}, which species might well have been norbornene. However, the ionization potential of the C_7H_{10} species was 8.6 v, compared to 9.05 v for an authentic sample of norbornene. It seems almost certain, therefore, that the C_7H_{11} radical observed was not the 2-norbornyl radical, but rather a rearrangement product of ring rupture.

The yield of C_7H_{11} radical from pyrolysis of 1-norbornylmethyl nitrite also was small, and the ionization potential, the behavior of the phenyl addition product, and the C_7H_{10} hydrocarbon resulting from hydrogen loss were not detectably different from those observed with 2-norbornylmethyl nitrite. The identity of both C_7H_{11} radicals could not be established.

The pyrolysis of 1-bicyclo[2.2.2]octylmethyl nitrite gave a good yield of C_8H_{13} radicals having an ionization

(1) Review: R. C. Fort, Jr., and P. von R. Schleyer in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, pp 283–370.

(2) G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967); W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, in press; P. von R. Schleyer, P. R. Isele, and R. C. Bingham, *ibid.*, in press.

(3) I. Tabushi, J. Hamuro, and R. Oda, private communication; R. C. Fort, Jr., 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S-165.

(4) R. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

(5) Commercially available (Eastman) 5-norbornene-2-methanol was reduced to give a mixture of *endo* and *exo* isomers, both of which should give the same radical.

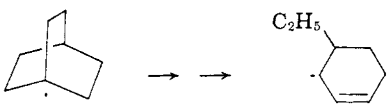
(6) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958). The precursor of this compound, 1-bicyclo[2.2.2]-octanecarboxylic acid, was prepared in 92% yield by a new way, the Koch–Haaf reaction (H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958)), on 1-norbornylcarbinol.

(7) N. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, **69**, 465 (1947).

(8) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *ibid.*, **83**, 3204 (1961).

(9) See D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

potential of 7.5 v. The concurrent pyrolysis of *t*-butyl perbenzoate gave a phenyl addition product whose 157/186 and 130/186 peak ratios were 1.2 and 0.6. For an authentic sample of 1-phenylbicyclo[2.2.2]octane,[10] these ratios were 0.55 and 1.05, respectively. It seems clear, therefore, that the C_8H_{13} radical observed was also a rearrangement product and not the 1-bicyclo[2.2.2]-octyl radical. A possible rearrangement is



There is some experimental evidence that the identity of the rearranged monocyclic radical is as shown. At higher furnace temperatures, the C_8H_{13} radical decomposed further by loss of a unit of mass 29, giving a compound whose ionization potential was the same as that of 1,3-cyclohexadiene. Moreover, the observed ionization potential of the C_8H_{13} radical is the same as that found recently[11] for 3- and 4-cyclohexenyl radicals. The change in ionization potential resulting from ethyl substitution (as in the radical above) would be expected to be negligibly small.

Although the attempted preparation of the desired radicals apparently was unsuccessful, this failure is instructive in that it shows that these bicyclic radicals are appreciably less stable toward ring rupture than monocyclic alkyl[8] and alkenyl[11] radicals, which could be produced in fair to good yields under the same conditions. Since the radicals themselves decompose faster than the nitrite esters at the temperatures employed, the activation energy for ring rupture in the radicals appears to be less than the 36 kcal/mole characteristic of nitrite decompositions.[12] Although it would be very desirable to obtain estimates for the energies of bridgehead free radicals in the gas phase by some other method,[1] the present work indicates not only that difficulties are to be anticipated, but that it will be highly important to establish that the radical studied is truly a bridgehead one and not some rearranged species.

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(10) Prepared by Dr. E. Wiskott by a Friedel-Crafts reaction on 1-hydroxymethylenenorbornane, using benzene as a solvent-reactant and $AlCl_3$ as the catalyst. The product, mp 72-74° (80% yield), gave only two sharp nmr peaks, at δ 1.75 (area 13) and at δ 7.27 (area 5).

(11) S. Pignataro, A. Cassuto, and F. P. Lossing, *J. Am. Chem. Soc.*, **89**, 3693 (1967).

(12) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1958.

T. McAllister, Z. Dolešek, F. P. Lossing
Division of Pure Chemistry
National Research Council, Ottawa, Canada

Rolf Gleiter, Paul von Ragué Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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Two Different Tetrahedral-Octahedral Coordination Equilibria for Nickel(II) in Molten Zinc Chloride-Cesium Chloride Mixtures

Sir:

It has long been known that nickel(II) and some other transitional metal ions contained in certain binary molten chloride salt solvents may occur as an equilibrium mixture of two coordination forms.[1] In the case of nickel(II), one of these forms has a distribution of coordination geometries that on the average is more or less tetrahedral, while the other is more or less octahedral. We report here the novel fact that solute nickel(II) in molten mixtures of zinc chloride and cesium chloride has two such tetrahedral-octahedral coordination equilibria, one of which occurs in melts containing about 50-70 mole % zinc chloride and the other in about 92-100 mole % zinc chloride.

Figure 1a shows the large change in formal absorptivity of dilute solutions of nickel chloride in molten zinc chloride-cesium chloride mixtures as the solvent composition is progressively varied from 50 to 72 mole % zinc chloride. At 50 mole % the spectrum is mostly that for a more or less tetrahedral coordination geometry. Upon increasing the zinc chloride content of the solvent, however, the tetrahedral bands decrease in intensity while octahedral bands grow in. At 72 mole % zinc chloride the spectrum is mostly that of a more or less octahedral coordination, and only traces of the strongest tetrahedral bands remain.

For the above spectra the formal absorptivity, ϵ_f, at any solvent composition is approximately the sum of a purely tetrahedral spectrum, ϵ_T, and a purely octahedral spectrum, ϵ_O, over the wavenumber range 5000-21,000 cm^{-1}. That is, $\epsilon_f = x\epsilon_T + (1 - x)\epsilon_O$, where x is a function of solvent composition but not wavelength, while ϵ_T and ϵ_O are composition invariant. Such a set of spectra is said to be internally linear. Exact internal linearity in the present case would signify that there are only two coordination geometries and that the spectrum of each is unaffected by solvent composition. The small deviations from internal linearity which were observed mean either that the spectra of the components are slightly sensitive to solvent composition or else that there are small amounts of additional species. Clearly we are dealing here with what is mostly a two-species tetrahedral-octahedral equilibrium in which octahedral geometry is favored by increasing the zinc chloride content of the solvent.

Between 72 and 92 mole % zinc chloride, the nickel(II) spectrum (not shown) changes only in minor ways, but as the zinc chloride content increases from 92-100 mole % (shown in Figure 1b) the octahedral bands reverse their direction of change and grow progressively weaker while simultaneously a new set of tetrahedral bands grows in. As before, this set of spectra is nearly internally linear so that we are dealing with a tetrahedral-octahedral equilibrium except that now tetrahedral geometry rather than octahedral geometry is favored by increasing the zinc chloride content of the

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(1) See, for example, C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958); C. K. Jørgensen, *Mol. Phys.*, **1**, 410 (1958); D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962); H. A. Øye and D. M. Gruen, *Inorg. Chem.*, **4**, 1173 (1965); C. A. Angell and D. M. Gruen, *J. Phys. Chem.*, **70**, 1601 (1966).