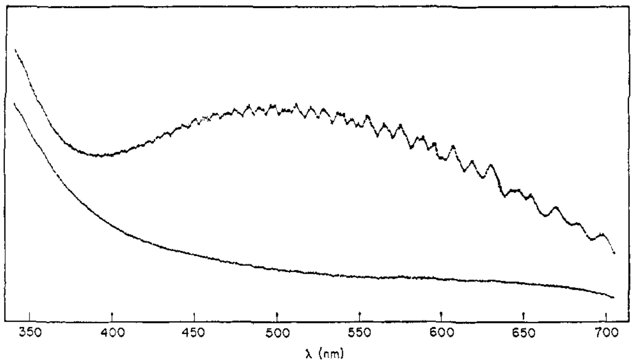

Figure 1. The absorption spectrum of γ-irradiated crystalline acetonitrile-d_3 at 77°K. Upper and lower spectra were recorded before and after photobleaching with visible light from the IR2 lamp of the Cary 14 spectrophotometer. The thickness of the optical cell was 0.1 cm and the γ-irradiation dose was 1 Mrad (6.2×10^{19} eV g^{-1}). The ordinate refers to a linear optical density scale such that the difference between the two curves at 510 nm is 0.65. That portion of the spectrum which lies beyond 700 nm is not shown, since it could not be recorded with the Cary 14 spectrophotometer used in this experiment because of the sensitivity of the absorption band to photobleaching by the IR2 lamp. The red portion of the spectrum was recorded in separate experiments using a Cary 14R instrument.

from separations averaged over several successive bands. At the beginning of the progression there seems to be marked intensity alternation such that one or two bands are too weak to be clearly resolved. On the high energy side of the absorption envelope, the structure is ultimately lost in the region of 2.50×10^4 cm^{-1}. While the existence of overlapping progressions is not revealed in the present spectra, this possibility should not be excluded and a complete analysis must await the better resolution which should be obtainable at 4°K.

The magnitude of the observed separation (306 cm^{-1}) leaves little doubt that this frequency is associated with a bending vibration in the upper state. For neutral CD_3CN in the ground state, the C—C≡N bending frequency is 331 cm^{-1} as determined from infrared studies.[9] The existence of a long progression in the bending mode is frequently characteristic of a transition from a linear ground state of the molecule to a bent upper state.[10] Therefore, we infer that in the present case, the electronic transition involves the promotion of the electron, which is trapped between two CD_3CN molecules, to a vacant molecular orbital (probably π^*) of CD_3CN, thereby forming a negative ion which assumes a bent structure in its equilibrium conformation. This negative ion may be formed in an electronically excited state. Since the esr studies show that photobleaching in this absorption band leads to the formation of $CD_3\cdot$, it is likely that predissociation occurs in this upper state. A schematic representation of the paths for photobleaching and thermal recovery in terms of potential energy curves has been given elsewhere.[8]

Vibrational fine structure has also been clearly observed in the corresponding absorption spectrum of the trapped electron in acetonitrile-h_3, and a detailed comparison of this structure with that produced in CD_3CN is now in progress. We plan to extend this work to include acetonitrile-d_1 and acetonitrile-d_2. As reported previously,[4] the trapped electron in CH_3CN is not recovered after photobleaching.

It is impossible, of course, to generalize from the present observations for this rather well-defined system to the nature of the optical transition for solvated and trapped electrons in other molecular assemblies. However, this work does suggest that the upper state can be the negative ion of a solvent molecule instead of being considered as an excited state of the solvated or trapped electron in the potential energy well of the surrounding molecules.[2]

A fuller account of our studies[11] will be reported in due course.

Acknowledgments. We thank Professor J. E. Willard of the University of Wisconsin for the gift of thin Suprasil cells. We are also indebted to Professor J. E. Bloor of this Department for valuable discussions. Initial experimental work on this problem by Dr. M. A. Bonin is appreciated and we are grateful to Dr. G. P. Smith of the Oak Ridge National Laboratory for the use of a Cary 14R spectrophotometer in part of this work.

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[9] W. H. Fletcher and C. S. Shoup, *J. Mol. Spectrosc.*, 10, 300 (1963).

[10] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, D. Van Nostrand Co., Inc., Princeton, N. J., 1966, p 167 ff.

[11] This contribution is based on work to be described in the M.S. Thesis of L. Holloman, The University of Tennessee, 1970.

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Reference-Independent Nuclear Magnetic Resonance Solvent Shifts

Sir:

We introduce here a reference-independent nuclear magnetic resonance (nmr) solvent shift and report data for converting measurements made with either internal or external references to the new scale. Use of this scale avoids the uncertainties inherent in the usual procedure of reporting nmr solvent shifts relative to a necessarily arbitrary reference solute. To obtain reference-independent solvent shifts to the desired accuracy (0.01 ppm) it is essential to determine accurately the bulk susceptibility difference between the two solvents involved. This has been accomplished by devising a new technique for measuring the bulk susceptibility difference, which yields values considerably more accurate (by at least an order of magnitude) than are available by subtraction of published susceptibility values.

In measuring proton magnetic resonance solvent shifts as an aid to molecular structure determination,[1–4] it has become customary to use an internal reference (usually tetramethylsilane, TMS) in both solutions, and to express the results for the solute protons as shifts in their resonance positions relative to the reference peak. In the usual notation, such a solvent shift is defined as

$$\Delta_y{}^x = \delta(y) - \delta(x) \qquad (1)$$

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[1] P. Laszlo, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 3, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1967.

[2] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 5, 139 (1962).

[3] J. Ronayne and D. H. Williams, *J. Chem. Soc., C*, 2642 (1967).

[4] T. Ledaal, *Tetrahedron Lett.*, 1683 (1968).

Table I. Internally Referenced Solvent Shifts for Nonpolar Solutes in Carbon Tetrachloride and Benzene

Solute	Protons	Internal reference	$\Delta_{C_6H_6}^{CCl_4}$, ppm	$\bar{\Delta}_{C_6H_6}^{CCl_4}$, ppm
CH_4	CH_4	TMS	+0.087	+0.61
$(CH_3)_4C$	CH_3	TMS	+0.021	+0.54
$CH_2{=}CH_2$	CH_2	TMS	+0.10	+0.62
		CH_4	+0.01	+0.62
		$(CH_3)_4C$	+0.08	+0.62
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	Olefinic CH	TMS	−0.29	+0.23

Table II. Externally Referenced Solvent Shifts for TMS in Various Solvent Pairs

Solvent x	Solvent y	$\sigma_{sol}^{\perp}(y) - \sigma_{sol}^{\perp}(x)$, ppm ± 0.01	$\sigma_{sol}^{\parallel}(y) - \sigma_{sol}^{\parallel}(x)$, ppm ± 0.01	$\sigma_{loc}(y) - \sigma_{loc}(x)$, ppm ± 0.02	$\chi_v(y) - \chi_v(x)$, $\pm 0.003 \times 10^{-6}$
Carbon tetrachloride	Benzene	+0.67	+0.21	+0.52	$+0.073 \times 10^{-6}$
	Pyridine	+0.80	+0.23	+0.61	$+0.091 \times 10^{-6}$
	Carbon disulfide	−0.16	−0.12	−0.15	-0.006×10^{-6}
Cyclohexane	Benzene	+0.40	+0.44	+0.41	-0.006×10^{-6}
	Pyridine	+0.54	+0.46	+0.51	$+0.013 \times 10^{-6}$
	Carbon disulfide	−0.41	+0.11	−0.24	-0.083×10^{-6}

where $\delta(x)$ and $\delta(y)$ are the positions of the given proton resonance in solvents x and y, respectively, measured in parts per million from the reference peak in the direction of increasing nuclear screening. If we represent the total contribution of a liquid medium to the nuclear screening as

$$\sigma_{sol} = \sigma_b + \sigma_{loc} \qquad (2)$$

where σ_b is the bulk magnetic susceptibility contribution[5] and σ_{loc} is the sum of all "local" effects (*i.e.*, effects other than bulk susceptibility), then in terms of screening constants (1) becomes

$$\Delta_y^{x} = \sigma_{loc}(\text{solute, y}) - \sigma_{loc}(\text{ref, y}) - \sigma_{loc}(\text{solute, x}) + \sigma_{loc}(\text{ref, x}) \qquad (3)$$

where the suffixes in parentheses have the obvious meaning.

This internal referencing procedure has the advantage that bulk susceptibility effects, which are irrelevant for most diagnostic purposes, do not contribute to the observed shift. However, as has been recently emphasized by Laszlo, *et al.*,[6] it introduces an arbitrary element in the choice of the internal reference, which is particularly serious for the study of nonpolar solutes, where the solvent shifts observed are entirely similar in nature to the change in the screening of the reference protons. In Table I we give the results of measurements on several nonpolar solutes in carbon tetrachloride and benzene. For ethylene we find that three different internal reference compounds, all nonpolar and with tetrahedrally symmetric structures, give different values for $\Delta_{C_6H_6}^{CCl_4}$. For 2,5-dimethyl-2,4-hexadiene, which is also nonpolar and presumably does not form specific collision complexes with benzene,[1-4] the olefinic protons nevertheless show a large shift relative to the TMS reference.

Ideally one would like to measure the quantity

$$\sigma_{loc}(\text{solute, y}) - \sigma_{loc}(\text{solute, x})$$

for infinitely dilute solutions, which is reference-independent, and is in a convenient form for comparing with theoretical predictions.

In the alternative procedure of external referencing, the result is independent of the choice of reference, but contains a σ_b contribution which, prior to the present work, could not be obtained with the desired accuracy because of uncertainties in magnetic susceptibility values. We have eliminated the troublesome bulk susceptibility differences from our externally referenced measurements by taking advantage of the difference in sample geometry between two spectrometers, one (Varian HA-100) having a conventional iron electromagnet which applies the magnetic field perpendicular to the sample tube axis, and the other (Varian HR-220) a superconducting solenoid magnet which applies the field longitudinally. Assuming cylindrical samples of effectively infinite length, the bulk susceptibility contribution for the perpendicular orientation is[5]

$$\sigma_b^{\perp} = \frac{2}{3}\pi\chi_v \qquad (4)$$

and for the parallel orientation it is[7]

$$\sigma_b^{\parallel} = -\frac{4}{3}\pi\chi_v \qquad (5)$$

For infinitely dilute solutions of the internal reference in two solvents, examined with both field orientations, the total relative shifts are

$$\sigma_{sol}^{\perp}(y) - \sigma_{sol}^{\perp}(x) = \frac{2}{3}\pi[\chi_v(y) - \chi_v(x)] + \sigma_{loc}(y) - \sigma_{loc}(x) \qquad (6)$$

$$\sigma_{sol}^{\parallel}(y) - \sigma_{sol}^{\parallel}(x) = -\frac{4}{3}\pi[\chi_v(y) - \chi_v(x)] + \sigma_{loc}(y) - \sigma_{loc}(x) \qquad (7)$$

for the perpendicular and parallel orientations, respectively. Combining eq 6 and 7 we have

$$\sigma_{loc}(y) - \sigma_{loc}(x) = \frac{1}{3}[\sigma_{sol}^{\parallel}(y) - \sigma_{sol}^{\parallel}(x) + 2(\sigma_{sol}^{\perp}(y) - \sigma_{sol}^{\perp}(x))] \qquad (8)$$

In Table II are listed our results for TMS in various solvent pairs. The TMS concentrations (<1% v/v)

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(5) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).

(6) P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, **48**, 1732 (1968).

(7) J. K. Becconsall, *Mol. Phys.*, **15**, 129 (1968).

were effectively infinitely dilute for this solute; in each case the two solutions were compared by placing them in the two compartments of a Wilmad coaxial sample cell, spinning in the magnetic field.

If an internal reference is used, the operational definition of the reference-independent solvent shift (for which we suggest the notation $\bar{\Delta}_y{}^x$) is

$$\bar{\Delta}_y{}^x = \Delta_y{}^x + \sigma_{loc}(\text{ref, y}) - \sigma_{loc}(\text{ref, x}) \qquad (9)$$

The tabulated values of σ_{loc} differences for TMS (Table II) can be used in eq 9 to convert internally referenced solvent shifts $\Delta_y{}^x$ to reference-independent shifts $\bar{\Delta}_y{}^x$ (*e.g.*, see last column of Table I).

Where the solvent shift is measured by an external referencing procedure, one can use an alternative definition of $\bar{\Delta}_y{}^x$ as that shift obtained by subtracting the bulk susceptibility contribution for the appropriate solvent pair from the total observed shift.

By reporting $\bar{\Delta}_y{}^x$ rather than other more arbitrary forms of the solvent shift, comparison between results obtained with different referencing procedures is facilitated.

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Acid-Catalyzed Rearrangements of Cyclohexa-2,4-dien-1-ones. Competitive [1,2] and [1,5] Migrations[1]

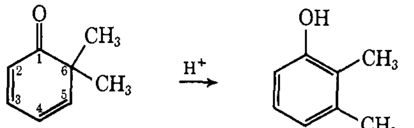
Sir:

The acid-catalyzed rearrangements of cross-conjugated cyclohexadienones have been extensively investigated.[2] In contrast, the rearrangements of linearly conjugated cyclohexadienones have not received much attention, except for the special, and very complicated, cases in which allyl groups migrate.[1,3] In the few reactions studied involving other migrating groups, the products of [1,2] shifts of the migrating group to C-5 have been obtained.[4]

I now wish to report that acid-catalyzed rearrangements of linearly substituted cyclohexadienones can result in either [1,2] or [1,5] shifts of the migrating group.[5] The type of rearrangement occurring is remarkably dependent on the nature of the migrating group.

Marvell and Magoon found that rearrangement of dienone **1** in acetic anhydride–sulfuric acid gave (after hydrolysis) a low yield of 2,3-dimethylphenol.[4a] Repetition of this reaction, both under the literature conditions and in acetic acid–sulfuric acid, showed that 2,3-dimethylphenol is indeed the only product detectable by vpc analysis.

In contrast, rearrangement of dienone **2** at 25° in acetic acid containing 1% sulfuric acid (reaction time = 20 min), or in aqueous dioxane catalyzed by HCl, gives 2-benzyl-6-methylphenol[7] as the only detectable rearrangement product.[8] Vpc analysis showed that no more than 0.5% of 3-benzyl-2-methylphenol[9] could have been produced during the reaction. Similarly, rearrangement of 6-benzyl-4-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one (**3**) in 0.5 *N* methanolic HCl gives 2-benzyl-4-*t*-butyl-6-methylphenol[9] and its methyl ether[9] as the only rearrangement products.



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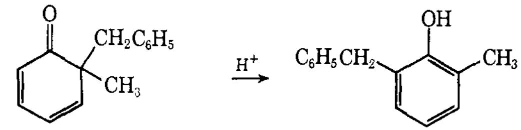
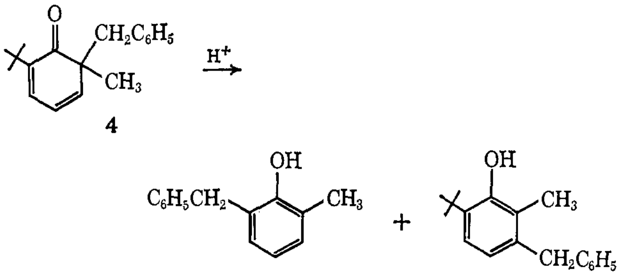


2

The rearrangements of **2** and **3** could proceed by migration of either the benzyl or methyl groups. However, rearrangement of **2** in 0.5 *N* HCl in 80% aqueous methanol has been found to be at least 10^3 times as rapid as that of **1**. This rate difference can only be explained if the benzyl group migrates during the rearrangement of **2**.

Migration of a benzyl group to C-2 can proceed even when C-2 is occupied by a *t*-butyl group. Rearrangement of dienone **4** in 2 *N* HCl in 80% aqueous methanol



results in partial elimination of a *t*-butyl group to give 2-benzyl-6-methylphenol and 5-benzyl-2-*t*-butyl-6-methylphenol[9] in the ratio 5:7.[10]

Migration of the benzyl groups in **2** and **4** to C-2 might, in principle, proceed by either direct [1,5] acid-catalyzed sigmatropic shifts (path a) or by a sequence of two Wagner–Meerwein shifts of the benzyl group—

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[1] Reactions of Cyclohexadienones. XXIII. Part XXII: *J. Amer. Chem. Soc.*, **91**, 2170 (1969).

[2] (a) B. Miller in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1968, pp 275–310; (b) A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 207–215 (1966).

[3] (a) J. Leitich, *Monatsh. Chem.*, **92**, 1167 (1960); (b) P. Fahrni, A. Habich, and H. Schmid, *Helv. Chim. Acta*, **43**, 448 (1960); (c) B. Miller, *J. Amer. Chem. Soc.*, **87**, 5115 (1965); (d) B. Miller, *Chem. Commun.*, 1435 (1968).

[4] (a) E. N. Marvell and E. Magoon, *J. Amer. Chem. Soc.*, **77**, 2542 (1955); (b) E. Schinzel and F. Wessely, *Monatsh. Chem.*, **86**, 912 (1955).

[5] Occurrence of [1,5] shifts have been previously reported[1,6] but only in dienones in which the "normal" [1,2] shifts are difficult or impossible.

[6] T. Suehiro, *Chem. Ber.*, **100**, 915 (1967).

[7] T. Schorigin, *ibid.*, **58**, 2028 (1925).

[8] All rearrangements of benzylated dienones give products of cleavage to the parent phenol as well as rearrangement products.

[9] These compounds have been independently synthesized by unequivocal methods.

[10] A small amount of 4-benzyl-2-*t*-butyl-6-methylphenol is also produced in this reaction, presumably by a twofold migration of the benzyl group to C-4.