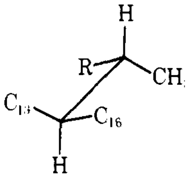
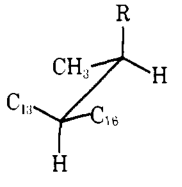
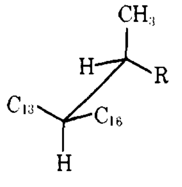
which staggered conformation, IIa, IIb, or IIc, is most stable. Thus, although IIa places the 20-H skew to the two largest groups on CH17, it also introduces a skew interaction between isohexyl and quaternary C-13, not present in IIc. Nes,[1] nevertheless, concludes that IIa is predominant and cites as evidence the ^{1}H NMR doublet due to 21-methyl which is at δ 0.91 ppm (from Me$_4$Si) in cholesterol but at 0.81 in 20-isocholesterol. Analogy is drawn between the 0.10-ppm upfield shift observed in these two epimers and the similar upfield shift for the *E* and *Z* isomers of $\Delta^{17(20)}$ olefins. It is argued that, when 21-methyl is toward C-13, its ^{1}H NMR is downfield from that in isomers in which it is toward C-16. The fallacy in using the olefin as a model can be seen from the ^{1}H NMR data on 20-methylcholesteryl systems. With two methyls now on C-20, conformational analysis of the system becomes unambiguous; IIIc, which places the sterically most demanding isohexyl group on C-20 skew to the two smallest groups on C-17, is clearly favored. It follows that the 21- and 28-methyls must be oriented as shown in IIIc, and yet they show singlets at 0.91-0.95 and 0.83-0.86 ppm! The ~0.10-ppm difference is thus not due to a conformational similarity to (*Z*)- and (*E*)-17(20)-dehydrocholesterol, but rather to the different magnetic environments each methyl is in owing to the adjacent chiral C-17. Even though isohexyl is larger than methyl, the barrier to rotation may be insufficient to freeze conformation. Indeed, it is found that, when the C-17 side chain is replaced by *tert*-butyl, it shows only a single sharp peak which broadens on cooling but gives no indication of splitting or even a shoulder down to −110 °C so that the barrier to rotation must be quite small. The *tert*-butyl compound, IVd, was synthesized by potassium *tert*-butoxide catalyzed methylation of aldehyde IVa[6] with excess methyl iodide in *tert*-butyl alcohol-tetrahydrofuran to give IVb, mp 158-160 °C, which was reduced by Huang-Minlon modification of Wolff-Kishner reduction to give IVc, mp 163-165 °C, which on acid hydrolysis (HCl in THF) gave in 28% overall yield IVd, mp 174-176 °C, NMR δ 0.95 (s, 9, *tert*-butyl). Satisfactory elemental and spectral analyses of all new compounds were obtained.



IIa

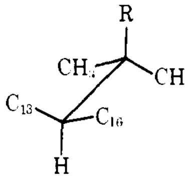


IIb

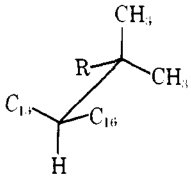


IIc

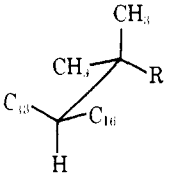
R = isohexyl



IIIa

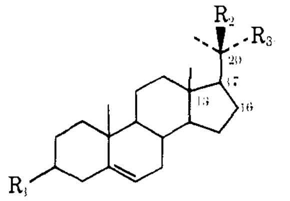


IIIb



IIIc

R = isohexyl



	R$_1$	R$_2$	R$_3$
IVa	OTHP	H	CHO
IVb	OTHP OTHP	Me CHO	CHO Me } mixture
IVc	OTHP	Me	Me
IVd	OH	Me	Me

The single resonance for *tert*-butyl in IVd shows that even a quaternary carbon at C-20 does not necessarily lead to conformational freezing of the C-17–C-20 bond. In support of his arguments for conformational freezing, Nes[2] cited Kohen's report[7] that there is sufficient barrier to rotation about C-17–C-20 to give rise to optical isomers in a molecule in which C-20 bears two methyls. However, full x-ray analysis[4] of Kohen's alleged C-20 epimeric pair shows them to be skeletal isomers.

A final word should be said about the dangers inherent in drawing conclusions about the population of ground-state conformers from the ratio of products which appear to be specifically derived from the different rotamers. As was pointed out by Hammett[8] long ago, the ratio of such products is independent of the equilibrium constant among ground-state conformers if conformational equilibration is rapid compared to the rate of reaction of the conformers. Thus, it is not valid to conclude that "approximately equal amounts of two conformers should exist at equilibrium which in turn would lead to approximately equal amounts of the *Z* and *E* products" as has been suggested for C-20 carbocations deprotonating to $\Delta^{17(20)}$-dehydrocholesterol.[3] Nor is it valid to conclude that the formation of both cholesterol and 20-isocholesterol by reduction of the $\Delta^{20(22)}$ double bond demonstrates the presence of two rotational isomers about C-17–C-20.[1]

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Synthesis and Characterization of the Dimolybdate Ion, $Mo_2O_7^{2-}$

Sir:

Although the dichromate ion, $Cr_2O_7^{2-}$, is a well-characterized species,[1] its molybdenum analogue has never been reported. Dichromate is formed as the predominent product upon stoichiometric acidification of aqueous CrO_4^{2-}, but acidification of aqueous M_2MoO_4 (M = Na, K, NH$_4$) at 25 °C fails to generate measurable concentrations of dimolybdate.[2] Instead, the heptamolybdate ion, $Mo_7O_{24}^{6-}$, is produced (eq 1). Compounds $M_2Mo_2O_7$ (M = K, Na, NH$_4$, and Ag) have been isolated from aqueous solution and anhydrous melts, but their structures are polymeric and do not contain discrete $Mo_2O_7^{2-}$ ions.[3] We report here the synthesis and structure of the dimolybdate ion as a tetrabutylammonium salt, and demonstrate that its stability relative to $Mo_7O_{24}^{6-}$ and MoO_4^{2-} (see eq 1) is determined by counterion interactions.

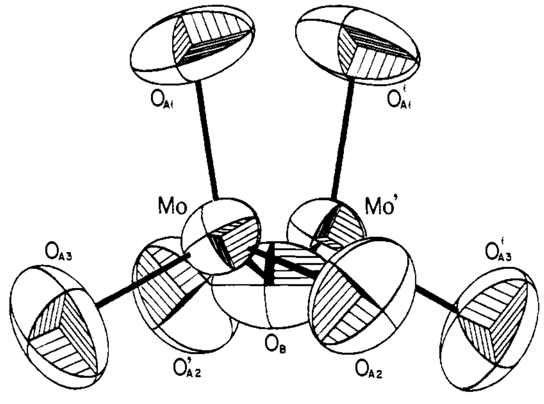

Figure 1. Perspective ORTEP drawing of the $Mo_2O_7^{2-}$ anion as observed in **1**, viewed perpendicular to the C_2 axis. All atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density. Atoms labeled with primes (′) are related to those without primes by the crystallographic twofold axis which passes through bridging oxygen atom O_B.

$$\begin{tikzcd}
4Mo_2O_7^{2-}(aq) + 4H_2O \\
8MoO_4^{2-}(aq) + 8H^+(aq) \arrow[u, "\times" marking] \arrow[d] \\
Mo_7O_{24}^{6-}(aq) + MoO_4^{2-}(aq) + 4H_2O
\end{tikzcd} \qquad (1)$$

Stoichiometric addition of $(n\text{-}C_4H_9)_4NOH$ to $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ in CH_3CN followed by addition of diethyl ether and cooling to 0 °C yields crystals of $[(n\text{-}C_4H_9)_4N]_2Mo_2O_7$ (**1**). Conductivity measurements and ^{17}O NMR spectra in CH_3CN indicate the presence of discrete $Mo_2O_7^{2-}$ ions in **1**, and an x-ray crystallographic study establishes the presence of the dimolybdate ion in the solid state. The large, well-shaped, transparent single crystals of **1** obtained as described above are monoclinic, space group $C2/c\text{-}C_{2h}^6$ (no. 15) with $a = 19.724\ (2)$ Å, $b = 14.000\ (1)$ Å, $c = 17.131\ (2)$ Å, $\beta = 120.966\ (7)°$, and $Z = 4$ ($[(C_4H_9)_4N]_2Mo_2O_7$ formula units); the observed and calculated densities are 1.170 and 1.173 g cm^{-3}, respectively. Three-dimensional x-ray diffraction data were collected on a computer-controlled four-circle Syntex P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The structure was solved using the "heavy atom" technique and the resulting structural parameters have been refined to convergence ($R = 0.048$ for 2110 independent reflections having $2\theta_{Mo\ K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms. Refinement is continuing with a data set three times as large (6952 reflections having $2\theta_{Mo\ K\bar{\alpha}} < 63.7°$) and a more sophisticated structural model which will incorporate hydrogen atoms with isotropic thermal parameters in addition to the anisotropic nonhydrogen atoms.

The structural analysis reveals that the crystal is composed of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $Mo_2O_7^{2-}$ anions as shown in Figure 1, in which two MoO_4 tetrahedra share a vertex. The anion possesses rigorous crystallographic C_2 symmetry. If all Mo-O_A bond lengths (Figure 1) and all O_A-Mo-O_A bond angles were equal and the mean planes of the two $(O_A)_3$ groupings were oriented normal to a linear Mo-O_B-Mo′ moiety in an eclipsed or staggered conformation, the anion would possess its maximum possible symmetry of D_{3h} or D_{3d}, respectively. Although the two equivalent $(O_A)_3$ groupings in the $Mo_2O_7^{2-}$ anion of **1** are oriented essentially perpendicular to their respective Mo-O_B bonds in a nearly eclipsed conformation, the Mo-O_B-Mo′ angle is 153.6 (5)° [4] and the dihedral angle between the mean planes of the two $(O_A)_3$ groupings is 24.7°. The two "eclipsed" tetrahedra in the $Mo_2O_7^{2-}$ anion of **1** are tilted toward the C_2 axis such that the $O_{A1} \cdots O_{A1}'$ separation of 4.134 (13) Å is considerably smaller than the $O_{A2} \cdots O_{A3}'$ (and $O_{A3} \cdots O_{A2}'$) separation(s) of 5.145 (9) Å. Hydrogen bonding is clearly not responsible for the observed anionic conformation in **1** since the lattice is devoid of solvent molecules. Also, no interionic contacts are significantly less than the sum of the appropriate van der Waals radii.

Average values for the six independent O-Mo-O bond angles and the three independent Mo-O_A bond lengths are 109.5 (3, 9, 16)° [4] and 1.716 (6, 4, 6) Å, respectively; the Mo-O_B bond length is 1.876 (2) Å. The five atoms (O_{A1}, Mo, O_B, Mo′, and O_{A1}') which would ideally lie in one of the two mutually perpendicular mirror planes of a C_{2v} structure are coplanar to within 0.11 Å and the dihedral angle between their least-squares mean plane and the plane determined by O_B and the midpoints of the $O_{A2} \cdots O_{A3}'$ and $O_{A3} \cdots O_{A2}'$ vectors is 84.7°. Oxygen atoms O_{A2}, O_{A3}, O_{A2}' and O_{A3}' are coplanar to within 0.15 Å.

Since mechanistic schemes[5,6] for molybdate polycondensation postulate initial formation of hydrated dimolybdate species such as $O[MoO(OH)_4]_2^{3-}$ and $HMo_2O_7(OH)^{2-}$, we have studied the interaction of **1** with water in nonaqueous solvents using ^{17}O NMR and IR spectroscopy. When **1** is dissolved in CH_3CN at 25 °C, ^{17}O NMR signals are observed at −715 ppm (terminal oxygens) and −248 ppm (bridging oxygen) relative to pure H_2O. Addition of water produces no measurable change in these chemical shift values, indicating that no substantial structural transformation has occurred. The characteristic IR absorptions observed for **1** in the solid state and in CH_3CN or DMF solution at 880 and 786 cm^{-1} are similarly unaffected by addition of water.

The unexpected stability of $Mo_2O_7^{2-}$ relative to $Mo_7O_{24}^{2-}$ in nonaqueous solution is easily shown to be a counterion effect. Addition of even small amounts of aqueous MX (M = Na, K, NH_4, $(CH_3)_4N$; X = Cl, Br) to **1** in CH_3CN or DMF yields immediate precipitation of $M_6Mo_7O_{24} \cdot nH_2O$. When **1** in DMF or CH_3CN is acidified with aqueous HCl, however, no $Mo_7O_{24}^{6-}$ can be detected by IR spectroscopy. Instead, absorptions characteristic of $\alpha\text{-}Mo_8O_{26}^{4-}$ and $Mo_6O_{19}^{2-}$ are observed.

We note that the unusual counterion effects reported here are analogous to those observed in the $Mo_8O_{26}^{4-}$ system.[7] In each case, large organic counterions favor the formation of polymolybdates containing tetrahedrally coordinated Mo^{VI} not observed in the presence of small counterions. We expect to find further examples of this behavior and are currently investigating other nonaqueous polymolybdate systems.

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are the average and maximum deviations from the average value, respectively.
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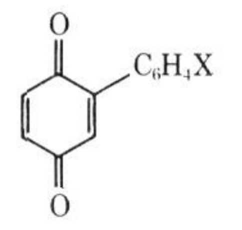
Crystal Growth by Nonaqueous Gel Diffusion[1]

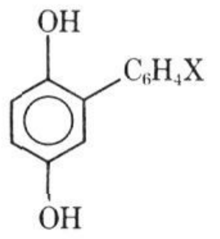
Sir:

Aqueous gel diffusion has been known since the end of the last century to be a superior method of crystal growth. It consists of the controlled growth of product crystals by diffusion of reactants together in a gel such as aqueous sodium silicate.[2] Since the method used *aqueous* gels, the low solubility in water of most organic compounds has excluded general applicability to such compounds.

In the course of an investigation[3] of 1:1 complexes (quinhydrones) of quinones such as **1** with hydroquinones such as **2**, we encountered much difficulty in obtaining single crystals because of a great tendency of the complexes to crystallize as fine powders or, alternatively, to form twinned crystals.[4]



1a, X = H
b, X = Cl



2a, X = H
b, X = Cl

This communication reports a method of preparing *nonaqueous* gels that permits the extension of crystallization by gel diffusion to a much wider range of compounds and which gives good results when other methods fail. The basis is the demonstration that Sephadex LH-20, an alkylated cross-linked dextran, forms suitable gels with aromatic hydrocarbons provided small amounts of an alcohol are present. The details of the procedure[5] are of great importance since the relative amounts of Sephadex and the other components must be so chosen that on mixing a satisfactory gel is obtained directly; otherwise the mixture must be discarded.

With this procedure, the complex **1a–2a** was readily obtained as single crystals with average dimensions 2 × 1 × 0.2 mm (Figure 1); attempts to obtain satisfactory crystals of this complex by other methods of crystallization or sublimation had failed. The method was equally successful with the complex **1b–2b.**

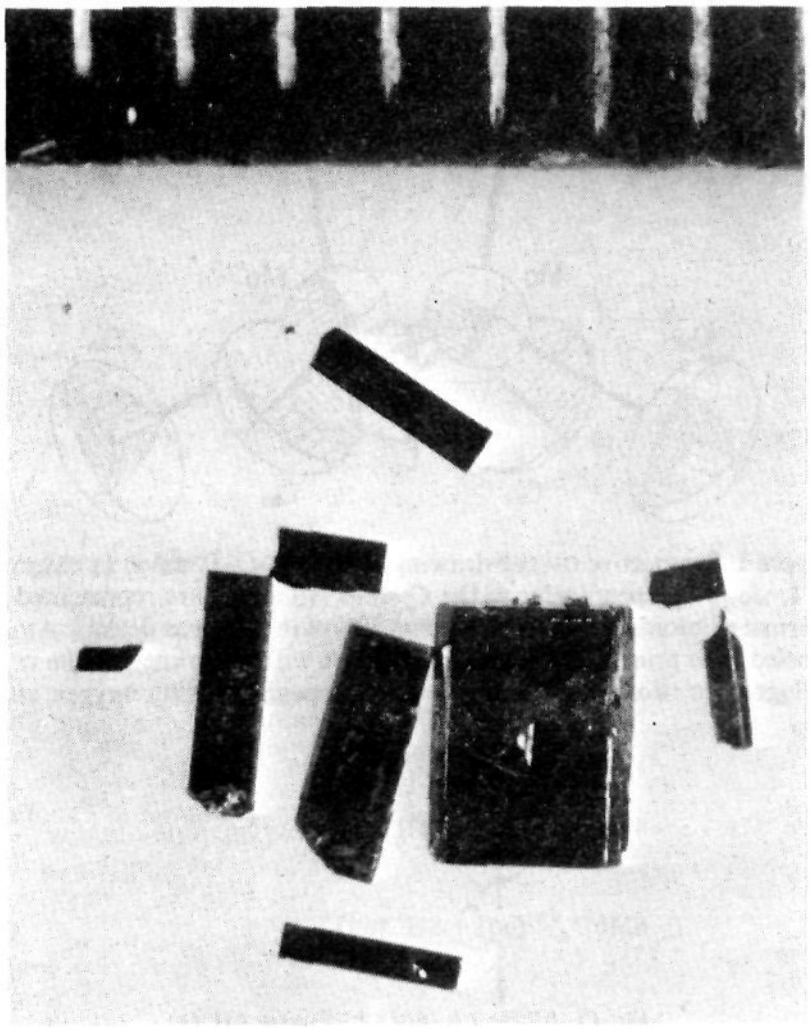


Figure 1. Crystals of the 1:1 complex **1a–2a** of 2-phenyl-1,4-hydroquinone-2-phenyl-1,4-benzoquinone grown by nonaqueous gel diffusion. A millimeter scale is shown at the top of the photograph.

When the chloroquinone **1b** was allowed to diffuse into a gel containing the unchlorinated hydroquinone **2a,** only the unchlorinated quinhydrone **1a–2a** was formed. A redox hydrogen transfer must have occurred in the gel during the diffusion process. An interesting point was that, in this case, there was formed a high proportion of untwinned crystals of **1a–2a,** whereas, when the same complex **1a–2a** was produced from **1a** and **2a,** many of the crystals of the product were twinned.

The nonaqueous gel diffusion method has also been successful with the naphthalene–picric acid complex[6] and with the phenol–benzoquinone (2:1) complex.[7]

It appears likely that crystallization with nonaqueous gels could have broad application to organic complexes. In addition, it seems probable that it can be adapted to the crystallization of single substances by diffusion of a poorer solvent into a gel prepared from a solution of the substance in a solvent in which it is more soluble.

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(5) Typically, to 0.65 g of hydroquinone **2a** in 3.8 mL of 3:1 toluene–methanol is added 1.7 g of Sephadex LH-20 (Pharmacia Fine Chemicals). The gel sets immediately. A solution of 0.25 g of quinone **1a** in 4 mL of the same solvent is poured on top of the gel and the container allowed to stand at room temperature. A black precipitate forms at the interface and, as the solutions slowly diffuse together, a deep coloration develops. Small well-formed crystals grow within the body of the gel after ~24 h. The crystals, after they have attained the desired size, are removed from the gel by washing with water.
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