orbit coupling constant for sulfur compared with oxygen.

(24) The preference of unhindered alkylthiylalkyl radicals for conformation **4** is best illustrated by the observation that the two hydrogens on the α-C in $H_2\dot{C}SCMe_3$ are nonequivalent.[21]

(25) It is possible that the low *g* values of $R_nMS\dot{C}(CMe_3)_2$ radicals are also, in part, a consequence of nonplanar geometry at the α carbon since it is known that the *g* factors of $(RO)_{3-n}\dot{C}H_n$[26] and of $F_{3-n}\dot{C}H_n$[27] decrease with increased bending at C_α. However, the $a^{^{13}C_\alpha}$ values for $R_nMS\dot{C}(CMe_3)_2$ radicals are of comparable magnitude to those of $R_nMCH_2\dot{C}(CMe_3)_2$ radicals[12] and most of the latter are believed to be planar[12] or close to it.[28] Moreover, a β sulfur is less effective than a β oxygen at inducing deformation at the α carbon.[22]

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Photoelectron Spectra of Sterically Congested Alkenes and Dienes

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Abstract: The He I photoelectron spectra of tetraisopropylethylene and several other tetrasubstituted ethylenes (including adamantylideneadamantane) have been recorded. Although NMR spectra of tetraisopropylethylene have indicated strong steric interactions between the alkyl groups, analysis of the vibrational structure in the photoelectron spectra of these compounds affords no evidence for unusual distortions of the double bonds arising from steric congestion. The values of ionization potentials, Franck-Condon band profiles, and Raman spectra of these compounds reinforce this conclusion. In contrast, the photoelectron spectra of three dehydro derivatives of tetraisopropylethylene do provide clear evidence of sterically induced skewing about the single bond joining the formally conjugated double bonds. The dihedral angles in the diene systems of 3,4-diisopropyl-2,5-dimethyl-2,4-hexadiene and 1,2-diisopropylidene-3,3,4,4-tetramethylcyclobutane have been estimated to be 83–97° and about 40°, respectively, from the PES data.

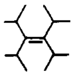
Introduction

Sterically crowded alkenes have attracted considerable interest because of the possibility that strong nonbonded interactions among bulky substituent groups may produce structural distortions about the double bond.[2] Sterically crowded dienes are of interest for similar reasons, and for the additional reason that atropisomerism may occur if severe nonbonded interactions prevent facile enantiomerization processes involving torsion about the central single bond.[3]

Continuing an investigation of the properties of sterically congested alkenes,[4] the present study examines the He I photoelectron spectra of tetraisopropylethylene (**1**), three of its dehydro analogues (**2, 3, 4**), two related congested alkenes (**5** and **6**), and adamantylideneadamantane (**9**).

Results and Discussion

The significant steric interactions in **1** are evident from its NMR spectra: both ^1H and ^{13}C NMR spectra exhibit two isopropyl methyl resonances and two isopropyl methine resonances, consistent with its expected conformation (Figure 1); from a line broadening analysis, the activation barrier to interconversion of the nonequivalent pairs of isopropyl groups at 24 °C has been calculated to be $\Delta G^{\ddagger} = 17$ kcal/mol.[4b,5]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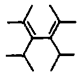
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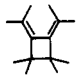
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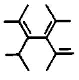
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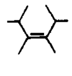
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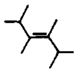
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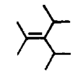
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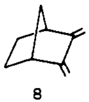
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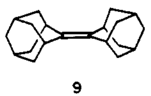
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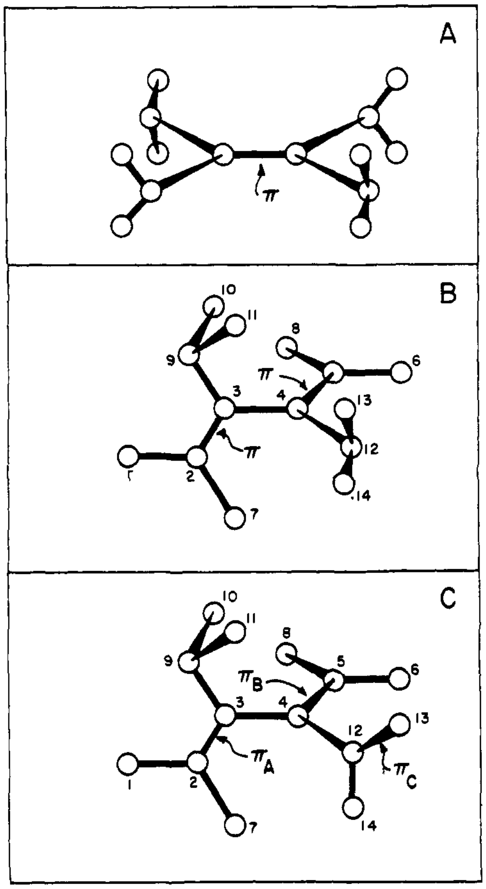

Figure 1. Proposed conformations of **1**, **2**, and **4**.

There are several precedents for using photoelectron spectroscopy to determine gross structural features of molecules in the gas phase.[2b,f,6] The He I photoelectron spectra of tetraisopropylethylene and several other tetrasubstituted alkenes have been recorded (Figure 2) and examined for evidence of nonplanarity in the double bonds. In each case, the 0 → 1 transition appears to be the strongest peak in the first band (π ionization), and the corresponding vertical ionization energies are recorded in Table I. All of the vertical ionization energies fall within the range expected for tetrasubstituted alkenes,[7] and there are no apparent anomalies in the pattern to suggest significant torsion about the double bond. For example, a plot of the IE's of trans-1,2-disubstituted dialkylethylenes vs. the IE's of the corresponding monoalkylethylenes (for Me, Et, *i*-Pr, *t*-Bu) gives a straight line. Similar plots for different polyalkyl substitution patterns are linear, allowing estimates of IE's for unknown compounds if additional alkyl groups behaved normally, i.e., if no torsion about the CC double bond occurs. Such an estimate for **1** gives an estimated value of 8.09 eV, within experimental error of the observed value. The unusually low IE of adamantylideneadamantane (7.84 eV) is actually quite unremarkable. Estimates performed as described above or by extrapolation of Grosjean et al.'s plot of alkene IE vs. number of alkyl substituents[7] give 7.95-7.98 eV for the IE of tetra-*tert*-butylethylene, if this molecule were planar. The similarity of these estimates to the value of the IE of **9** is expected for molecules with similar numbers of carbons in the alkyl groups. Both an experimental structure determined for crystalline **9**[8] and a molecular mechanics force-field optimization of the structure for the free molecule[2e] indicate a planar π system.

Also included in Table I are the double-bond stretching frequencies measured for the neutral molecules (Raman) and the radical cations (PES). The Raman stretching vibrations shift to lower frequency with increasing size of the substituents, paralleling trends reported for di- and trisubstituted olefins;[2c] the very small difference between **5** and **6** ($\Delta\nu = 2$ cm^{-1}) clearly shows that the steric interaction of two isopropyl groups is not capable of twisting the double bond, and the moderate shift observed on going from **5** or **6** to **1** ($\Delta\nu = 8$-10 cm^{-1}) is hardly suggestive of twisting in the tetraisopropyl compound.[9] Considering the experimental error, the differences between the vibrational frequencies measured for different radical cations (including ethylene) are generally insignificant, as is also the case for the changes in frequency produced by ionization. Thus, despite the heavy steric congestion indicated by the relatively large barrier to rotation of isopropyl groups in **1**, there appears to be no evidence here of unusual distortions in either the isopropyl-substituted molecules or their radical cations. The only change in the PE spectra upon increasing

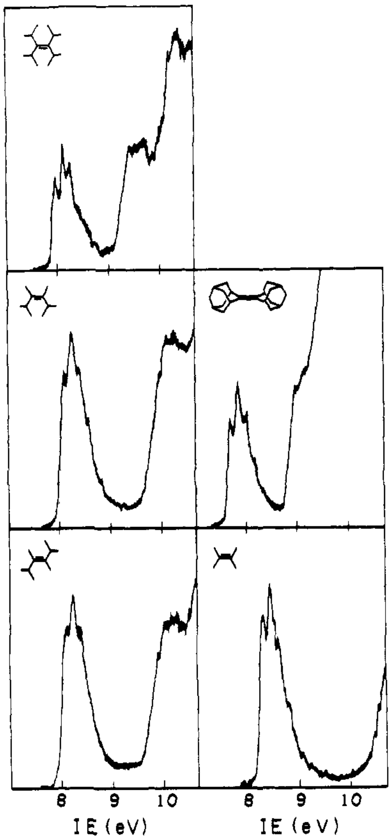

Figure 2. Photoelectron spectra of tetrasubstituted alkenes: **1**, **5**, **6**, **9**, and tetramethylethylene.

Table I. Vertical Ionization Energies and Double-Bond Stretching Frequencies in Tetrasubstituted Olefins and Their Molecular Ions

Compd	IE$_1$, eV	$\nu_{C=C}$ (M), cm^{-1}	$\nu_{C=C}$ (M$\cdot^+$), cm^{-1}	$\Delta\nu$, cm^{-1}
1	8.13	1638	1270 (±50)	368
5	8.27	1644	1230 (±50)	414
6	8.24	1646	1150 (±50)	496
7	(8.28)[a]	1657[b]		
2,3-Dimethyl-2-butene	8.46	165[c]	1300 (±50)	375
9	7.84	1657	1320 (±50)	337
Ethylene[d]	10.51	1623	1230 (±50)	393

[a] Estimated from ionization energies of **5** and **6** (this work) and data reported in ref 7. [b] Reference 10. [c] D. G. Rea, *Anal. Chem.*, **32**, 1638 (1960). [d] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970, p 166.

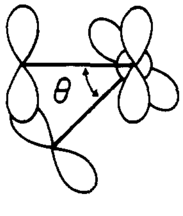

Figure 3. Definition of the dihedral angle (θ) in 1,3-dienes discussed in the text.

crowding is an increase in the relative intensity of the 0 → 2 vibrational bond, and perhaps also the 0 → 1 bond relative to the 0 → 0. The changes are not dramatic, however, and indicate very slight changes in the radical cation potential minimum relative to that of the ground state as crowding increases.

As in the case of **1**, steric congestion in the acyclic diene **2** again results in severely hindered internal rotations.[4a] The ^{1}H and ^{13}C NMR spectra of **2** indicate that the molecule has only C_2 symmetry, with a remarkably high barrier to rotation about the C(3)-C(4) bond; two nonequivalent isopropyl methyl resonances and only one isopropyl methine resonance are observed in the ^{1}H NMR spectra up to 195 °C, implying a high barrier to internal rotation, ($\Delta G^{\ddagger} > 26$ kcal/mol) at that temperature. The C_2 symmetry requires a skewing of the diene system, which is consistent with other spectroscopic data: (1) the C=C stretching frequency (1645 cm^{-1}) observed in the Raman spectrum of **2** is only slightly lower than that of **7**, indicating negligible conjugation of the double bonds; (2) the ultraviolet spectrum of **2** shows no λ_{max} above 200 nm (ϵ 4500 at 200 nm; apparent shoulder ~235 nm, ϵ <500), while its cyclized analogue **3**, where ring closure constrains the dihedral angle θ (Figure 3) between the two π bonds, exhibits λ_{max} 253 nm.[11] Analysis of the photoelectron spectra of **2** and **3** not only affords further evidence for the skewed conformation of **2**, but also allows an estimation of the dihedral angles (θ) in the π systems of **2** and **3**.

As mentioned above, the first ionization energy of **1** (IE$_1$ = 8.13 eV) corresponds to ionization from the highest occupied π orbital; the σ onset occurs at about 9.2 eV. On going to the acyclic diene **2** (Figure 4), three points may be noted. First, the σ onset is shifted to about 10.0 eV. Second, the average energy of the π levels has been lowered to 8.33 eV (IE$_1$ = 8.22 eV, IE$_2$ = 8.43 eV). Both of these features may be attributed to the "inductive" effect of introducing a second site of unsaturation into the carbon skeleton.[12] Finally, there is a splitting in the first band of the spectrum; the magnitude of the splitting (ΔE = 0.21 eV = 1694 cm^{-1}) precludes its being assigned to any vibration, and it is attributed instead to a small, but nonzero, conjugative interaction between the two π-bonds.

Inasmuch as butadiene in the gas phase is planar, the difference in the energies of its π levels, ΔE = 2.41 eV, may be taken as an upper limit to any splitting due to classical conjugation.[6a,13] Assuming a simple dependence of the splitting (ΔE) on the cosine of the dihedral angle (cos θ),[23] it is possible to estimate the dihedral angle in the π system of **2**:

$$\Delta E = 0.21 \text{ eV} = (2.41 \text{ eV})(\cos\theta)$$

$$\theta \simeq 85^\circ \text{ (or } 95^\circ)$$

Since cos θ is near zero and changes slowly for θ near 90°, the calculated value of θ is not particularly sensitive to the choice of reference compound for an estimate of ΔE in planar **2**. Thus, if the π-orbital splitting (Δ = 1.82 eV) in diisopropylidenetetramethylcyclobutane (**3**), which is almost certainly not planar (vide infra), is taken as a lower limit to the conjugative interaction in a planar 1,3-diene, the dihedral angle in **2** is calculated to be θ = 83.4° (or 96.6°). Although it is impossible to state whether the π system in **2** prefers a cisoid (θ = 83-85°) or a transoid (θ = 95-97°) conformation, the overriding point which emerges is that the two double bonds (C(2)-C(3) and C(4)-C(5)) are essentially perpendicular, as shown in Figure 1. For comparison, the somewhat less hindered acyclic diene, 2,3-diisopropylidene-1,4-butanediol has been found to have a dihedral angle of 104.8° by an x-ray structure determination.[14]

Figure 4. Photoelectron spectra of congested dienes **2** and **3** and triene. **4**.

The first two bands in the spectrum of **3** (Figure 4) again correspond to the π levels (IE$_1$ = 7.49 eV, IE$_2$ = 9.31 eV). The small shift in their average energy—8.40 eV in **3**, vis-à-vis 8.33 eV in **2**—can be traced to the effect of ring closure.[1,16] Not surprisingly, the splitting in **3** (Δ = 1.82 eV) is much greater than that in **2**. Significantly, however, the splitting is substantially less than that expected for a planar diene. It is also noteworthy that the vibrational structure in the first band of **3** corresponds to a lower stretching frequency (ν = 1370 cm^{-1}) than is observed in the radical cations of other conjugated dienes.[6a,13,16] The steric repulsions inherent in a C_{2v} conformation (planar ring, planar diene) could reasonably be expected to produce some ring puckering. Indeed, x-ray structure determinations have been carried out for several 1,2-dimethylenecycloalkenes substituted by two or four exo substituents, and dihedral angles of 18-52° have been found in these compounds.[3c,17] Exactly such a distortion has been proposed to account for the facility with which **3** undergoes a photolytic antarafacial 1,5-hydrogen shift.[11c] An additional measure of nonplanarity in the diene system of **3** is suggested by uv absorption data: in 2,3-dimethylenenorbornane (**8**), where the bridged bicyclic carbon skeleton should impart greater rigidity to the diene moiety, the absorption maximum occurs at λ_{max} 248 nm;[18] however, **3** exhibits a maximum at only λ_{max} 253 nm,[11] despite the presence of the four additional methyl substituents at the diene termini.[19] Again assuming a simple cos θ dependence for ΔE and using butadiene as the reference system, the dihedral angle in the diene system of **3** can be estimated to be $\theta = 40°$.

The introduction of the third double bond in **4** renders all three π bonds (π_A, π_B, π_C, see Figure 1) nonequivalent. However, the new presence of π_C does not significantly relax the steric constraints on the conformation of the carbon skeleton. The barrier to internal rotation about the C(3)-C(4) single bond is still remarkably large ($\Delta G^{\ddagger} = 24$ kcal/mol at 180 °C).[4a] Moreover, **4** exhibits no absorbance maximum above 200 nm (ϵ 3000 at 200 nm; apparent shoulder ~ 230 nm, ϵ 1000), while conjugated dienes absorb at much longer wavelengths (vide supra) and other cross conjugated trienes have absorbance maxima in the range 234-285 nm.[20] Thus, π_C is expected to be skewed by 85-95° relative to π_B, which in turn will remain similarly skewed relative to π_A.

The resultant arrangement (Figure 1C) allows the following assignment of the spectrum of **4** (Figure 4). The first three bands roughly correspond to π_A, π_B, and π_C, respectively. The assignment of the third ionization energy ($IE_3 = 9.39$ eV) to π_C is straightforward, as π_C is only disubstituted. The slight stabilization of π_B ($IE_2 = 8.51$ eV) on going from **2** to **4** may be attributed to the "inductive" effect of π_C operating in the absence of any major conjugative interaction between π_B and π_C. In contrast, the interposition of an extra σ bond between π_A and π_C should attenuate the "inductive" effect of the latter, while overlap of the terminus of π_C at C(12) with the terminus of π_A at C(3) permits a "through space" interaction which destabilizes π_A ($IE_1 = 8.14$ eV) relative to the π levels in **2**.[21] Although quantitative attempts at estimates of dihedral angles in **4** would be treacherous, it is reasonable to conclude from the PES spectrum that both alkene-alkene dihedral angles are near 90°.

Conclusion

The photoelectron spectra reported here strengthen earlier conclusions[9] that even quite severe crowding of substituents about an alkene π bond is not relieved to any significant extent by torsion about the π bond. Even in the radical cation formed by π ionization, no large differences in vibrational frequencies are observed, so that no large changes from the planar geometry are likely. In sterically congested dienes, the small preference for planarity observed in butadiene is overcome, and the preferential geometry is near 90°, resulting in very slight interactions between π levels.

Experimental Section

^{1}H NMR spectra were recorded on a Varian A-60 NMR spectrometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D magnetic sector instrument. Laser Raman spectra were recorded on a Jarrell-Ash 25-300 Raman spectrometer with a 488.0 nm exciting line from a Carson 150-FB argon laser. He I photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer, with xenon and argon as calibration standards.

Materials. Compound **9** was prepared and purified by a published procedure.[22] Compound **1**, prepared by a published procedure[4b,5] and purified by sublimation and subsequent recrystallization from chloroform, gave only one peak by GLC on a 15 ft × ¼ in. column of 20% SE-30 on Chromosorb P. Compounds **2**, **3**, and **4** were prepared by published procedures[4a,11] and purified by preparative GLC on the above column. Titanium trichloride was purchased from ROC-RIC Inc. and from Ventron Corp. and was handled under nitrogen in a glove bag. 3-Methyl-2-butanone was purchased from Aldrich Chemical and was used without further purification. Tetrahydrofuran was freshly distilled from lithium aluminum hydride.

2,3,4,5-Tetramethyl-3-hexene. Lithium aluminum hydride (1.2 g, 0.03 mol) was added to a magnetically stirred, ice-cooled suspension of 12.5 g of titanium chloride (0.08 mol) in 120 ml of dry tetrahydrofuran under nitrogen. After the evolution of gas had subsided, the black suspension was allowed to warm to room temperature and 2.7 g of 3-methyl-2-butanone (0.03 mol) in 5 ml of dry tetrahydrofuran was added. The reaction mixture was refluxed for 4 h, poured into a separatory funnel containing 200 ml of ice-water slush, and extracted with four 50-ml portions of pentane. The combined pentane extracts were washed with twenty 100-ml portions of water, followed by washings with 100-ml portions of 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution. The pentane solution was dried over anhydrous magnesium sulfate and the pentane was removed under reduced pressure to afford 0.5 g of clear oil, which was shown by GLC on an open tubular didecyl phthalate column (50 ft × 0.02 in.) to consist primarily (~90%) of a mixture of the two isomers of 2,3,4,5-tetramethyl-3-hexene (0.003 mol, 20% yield). The mixture of isomers showed two peaks, retention times 35.5 and 38 min, in the ratio 1.2:1 as measured by GLC on a column (10 ft × ¼ in.) of 10% diisodecyl phthalate on 60/80 Chromosorb P (DMCS treated) at 120 °C with a helium flow of 20 cm^3/min. These peaks were assigned to the *E* and *Z* isomers (**6** and **5**), respectively, on the basis of the Raman absorptions (Table I above) measured on neat samples collected by preparative glc. (*E*)-2,3,4,5-Tetramethyl-3-hexene: ^{1}H NMR ($CDCl_3$) δ 0.92 (d, $J = 7$ Hz, $(CH_3)_2C$), 1.52 (s, $CH_3C{=}C$), 2.83 (septet, $J = 7$ Hz, CH); mass spectrum (70 eV), *m/e* (relative intensity), 140 (20), 125 (13), 97 (94), 83 (44), 81 (15), 70 (66), 69 (76), 67 (23), 57 (41), 55 (100), 53 (32), 43 (66), 42 (18), 41 (97), 39 (21). (*Z*)-2,3,4,5-Tetramethyl-3-hexene: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, $J = 7$ Hz, $(CH_3)_2C$), 1.50 (s, $CH_3C{=}C$), 2.97 (septet, $J = 7$ Hz, CH); mass spectrum (70 eV), *m/e* (relative intensity), 140 (12), 125 (7), 97 (100), 83 (23), 81 (8), 70 (33), 69 (67), 6 (13), 57 (24), 55 (95), 53 (17), 43 (37), 41 (92), 39 (36).

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Carbon-13 Magnetic Resonance Spectra of C-Nucleosides. 3.[1a-c] Tautomerism in Formycin and Formycin B and Certain Pyrazolo[4,3-*d*]pyrimidines

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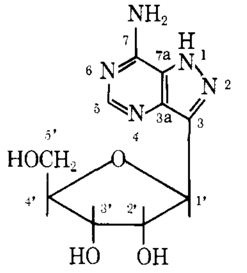
Abstract: Selected pyrazolo[4,3-*d*]pyrimidine heterocycles and nucleosides were examined by carbon-13 NMR spectroscopy. The carbon chemical shifts and line widths of certain aromatic and carbohydrate carbons were observed to be a function of temperature. Through an analysis of the carbon chemical shift data, the tautomeric populations of the C-nucleosides formycin (**4**) and formycin B (**10**) were determined. The prototropic N(1)H $\rightleftharpoons$ N(2)H process which occurs in the pyrazole portion of the heterocyclic aglycon was the only tautomeric process observed in these nucleosides and certain derivatives. The percentage of the N(2)H tautomer, a higher energy species, was shown to be dependent on the substituent at C7 in the pyrimidine portion of the pyrazolo[4,3-*d*]pyrimidine ring.

I. Introduction

Since the isolation[2,3] and characterization[4,5] of the C-nucleoside antibiotics formycin (**4**) and formycin B (**10**) from *Norcardia interforma,* numerous reports have appeared in the literature describing some of their biological and physicochemical properties.[1a,6] Formycin and formycin B, unlike their isomeric purine nucleoside counterparts adenosine and inosine, possess a C-glycosyl linkage. This unique linkage allows prototropic tautomerism to take place in the five-membered ring portion of the heterocyclic aglycon in contrast to adenosine or inosine. Two preliminary communications[1a,7] have recently described the effect such tautomeric processes have on the ^{13}C NMR spectra of formycin and formycin B. We have now extended our probe of all tautomeric processes in **4** and **10** by examining their ^{13}C NMR spectra as well as the ^{13}C spectra of certain model pyrazolo[4,3-*d*]pyrimidine heterocycles and nucleosides (Table I) in two solvents, i.e., dimethyl sulfoxide (Me_2SO) and hexamethylphosphoric triamide {[$(CH_3)_2N]_3PO$ or HMPT}, and as a function of temperature. Because of their physical properties, these solvents enabled us to evaluate tautomeric equilibria from an analysis of carbon chemical shift data in the fast and slow exchange rates.



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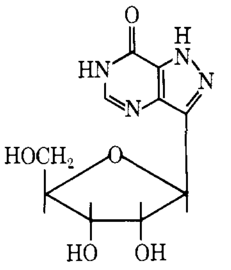

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II. Experimental Section

Carbon-13 NMR spectra were obtained with a Varian XL-100-15 spectrometer equipped with a Varian 620f computer for Fourier transform operation. Compounds were dissolved in dry, spectroquality Me_2SO or $[(CH_3)_2N]_3PO$ and the concentrations for each compound studied are provided in the appropriate tables. Cyclohexane was selected as an internal reference for this study since its chemical shift was observed to be nearly independent of temperature.[8] All carbon chemical shifts were observed with respect to the internal dioxane (ca. 2% v/v) line and then converted to the cyclohexane scale. The conversion formula (1) used for Me_2SO solutions is as follows:

$$\delta_{\text{cyclohexane}} = (\delta_{\text{dioxane}} + 40.0_0\ \text{ppm}) + 1.0 \times 10^{-3}T \qquad (1)$$

where T is the temperature in degrees centigrade. A second formula (2) allows the conversion to the Me_4Si scale:

$$\delta_{Me_4Si} = (\delta_{\text{dioxane}} + 66.2_8\ \text{ppm}) + 2.0 \times 10^{-3}T \qquad (2)$$

The conversion formulas (3 and 4) for $[(CH_3)_2N]_3PO$ solutions are as follows:

$$\delta_{\text{cyclohexane}} = \delta_{\text{dioxane}} + 40.2_3\ \text{ppm} \qquad (3)$$

$$\delta_{Me_4Si} = (\delta_{\text{dioxane}} + 67.2_5\ \text{ppm}) + 1.2 \times 10^{-3}T \qquad (4)$$

It should be pointed out that the chemical shift of dioxane in $[(CH_3)_2N]_3PO$ is independent of temperature and this accounts for the absence of the temperature term in eq 3. The ^{1}H NMR spectra were determined using either a Varian 56/60 or XL-100-12 spectrometer. The methods used for the synthesis of pyrazolo[4,3-*d*]pyrimidine heterocycles and nucleosides can be found in Table I.

III. Results

Carbon-13 NMR spectra were determined using noise de-