a doublet (5.43 Hz) of triplets (1.45 Hz) at δ 6.32 (2 H), a doublet (2.50 Hz) of doublets (1.45 Hz) at δ 3.01 (4 H), and singlets at δ 1.32 (3 H), 1.29 (6 H), and 1.27 (3 H). ^{13}C NMR (proton coupled) showed a singlet at δ 145.1 (>C=), a doublet at δ 131.3 (–CH=), a triplet at δ 38.9 (CH_2), a singlet at 34.8 (>CMe_2), and quartets at δ 31.5, 30.1 (double intensity), and 28.7 (CH_3's). Major mass spectral peaks occurred at *m/e* 212, 197, 182, 167, 152, 141, 139, 128, 115, and 89. All of these data are now readily rationalizable in the light of the X-ray result. The Raman spectra of the product were essentially identical in CH_2Cl_2 solution and in the solid state.

(7) Clear, colorless needle shaped crystals, mp 79–80.5 °C, were obtained by vacuum sublimation and were sealed in Lindemann capillaries. Preliminary X-ray data established the space group as $P2_12_12_1$ (No. 19) with four formula units ($C_{16}H_{20}$) in a cell of dimensions $a = 11.928$ (3), $b = 6.746$ (2), and $c = 16.127$ (5) Å. Three-dimensional data were collected on a Syntex $P2_1$ diffractometer using Mo Kα radiation to a maximum 2θ of 52°. The structure was solved using the acentric direct methods routines of the program SHELX, the best *E* map revealing all of the nonhydrogen atoms. The hydrogen atoms were located in subsequent difference maps and indicated disorder at the 1, 3, 5, and 7 positions. Block-diagonal least-squares refinement using 1085 observed reflections ($I/\sigma(I) \geq 2.0$) and with the carbon atoms having anisotropic temperature factors, converged to a final R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|^2$) of 0.045 and weighted R ($= [\Sigma\omega||F_o| - |F_c||^2/\Sigma\omega|F_o|^2]^{1/2}$) of 0.032 where the weights used were $[1/\sigma(F)]^2$. The molecule is completely planar in the crystal possessing a noncrystallographic center of symmetry and overall D_{2h} symmetry, although this arises from considering the lattice to contain an equal distribution of the dimers **2a** and **2b** with C_{2h} and C_{2v} symmetry, respectively. Bond distances and angles are close to accepted values (Table I).

(8) Attempts to separate these isomers by TLC on alumina or silica gel have, thus far, proven unsatisfactory.

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σ and π Components of Substituent Effects in Saturated Systems. Monosubstituted Methanes

Sir:

A molecular orbital description of methane utilizes one MO derived from the C 2s orbital and three degenerate molecular orbitals derived from the C 2p orbitals. These MO's differ in energy by 10 eV and have the proper symmetry for a system in the T_d point group.[1] When a substituent is introduced, the maximum degeneracy is reduced to 2. The methyl group 2s and 2p orbital directed toward the substituent form σ-type MO's. The other two 2p orbitals lead to a pair of π-type degenerate MO's. A substituent such as fluorine will interact with the methyl group orbitals to give a pair of low energy s-σ orbitals, a pair of p-σ orbitals (one of which will be antibonding), and two sets of degenerate π-type orbitals.

This description of a monosubstituted methane suggests that there should be σ and π interactions in a fashion similar to that in benzene. A π interaction involving back-bonding by the fluorine lone pairs has been suggested,[2] but the ionization potential of methyl fluoride has been interpreted as indicating a minimal interaction of this type.[3] In order to explore the possible importance of such interactions, extended basis set calculations have been carried out for a variety of monosubstituted methanes.

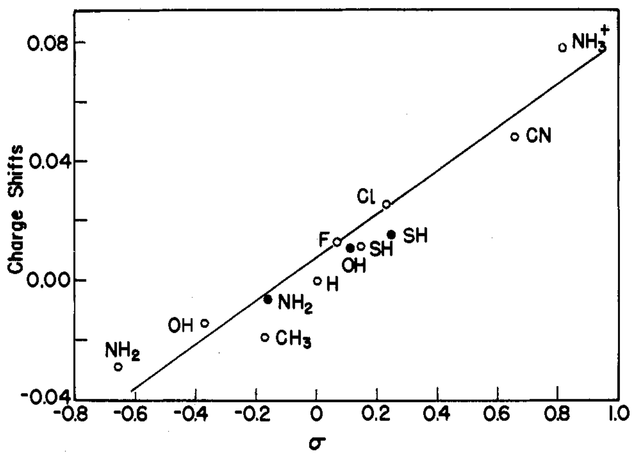

Figure 1. Relation between H charge shifts and σ for CH_3X. With X = NH_2, OH, and SH, the open circles represent hydrogens trans to lone pairs and are plotted against σ_p. The closed circles represent hydrogens trans to X–H bonds and are plotted against σ_m.

Table I. Calculated Charge Shifts at Hydrogen

X	q_H[a]	Δq_H	X	q_H	Δq_H
O^-	1.028	−0.131	NH_2	0.925[b]	−0.029
S^-	0.981	−0.084		0.902[c]	−0.005
CH_3	0.915	−0.019	OH	0.910[b]	−0.014
H	0.896	(0.000)		0.885[c]	+0.012
F	0.883	0.013	SH	0.885[b]	0.011
Cl	0.871	0.026		0.882[c]	0.015
CN	0.848	0.048			
NH_3^+	0.818	0.078			

[a] The hydrogen electron density plus one half the electron density in the C–H bond function. [b] Hydrogen trans to a lone pair. [c] Hydrogen trans to an X–H bond.

It has been found that the 4-31G basis set, when augmented by bond functions (an s orbital at the midpoint of C–H bonds and a set of s and p orbitals at the midpoint of C–X bonds), leads to a good electron density distribution for methane, methyl fluoride, and methyl chloride.[4] This basis set has been used for the present calculations. In order to be able to use a Mulliken population analysis[5] to give hydrogen charge shifts caused by substituents, a constant geometry was used, with tetrahedral angles about the methyl carbon and 1.09-Å C–H bond lengths. Most methyl compounds have geometries close to these values (±1°, ±0.005 Å).[6] The remaining geometrical parameters were taken as the experimental values.[6] The results are summarized in Table I.

The small effect of fluorine compared with chlorine and the electron-releasing effect on a hydroxy or amino group for the methyl hydrogens trans to the lone pairs provide clear evidence for a π interaction. With all substituents except methyl, the σ inductive effect will transfer electron density from the methyl group to the substituents and this will be opposed by the π interaction. The calculated effects are, in fact, very close to those observed with benzene derivatives for which σ and π effects are well established. This is clearly shown in Figure 1 in which the charge shift at hydrogen is plotted against the Hammett σ values. In the case of X = OH, NH_2, and SH, there are two charge shifts for the methyl hydrogens. The shift for the hydrogens of the C–H bonds which overlap the X lone pairs are plotted against σ_p, whereas the shift for the other hydrogens is plotted against σ_m. The σ_p values were used for the other substituents. The only substituent with a large deviation from linearity is X = O^-, and here solvent effects would be expected to be particularly important in determining the value of σ.[7]

The effect of substituents on the valence orbital energies is also of interest (Figure 2). The lowest energy MO corresponds to a C–X s-σ bond, and the energies change in accord with the electronegativity of the substituent. The energies of the other MO's change relatively little, except when a molecular charge

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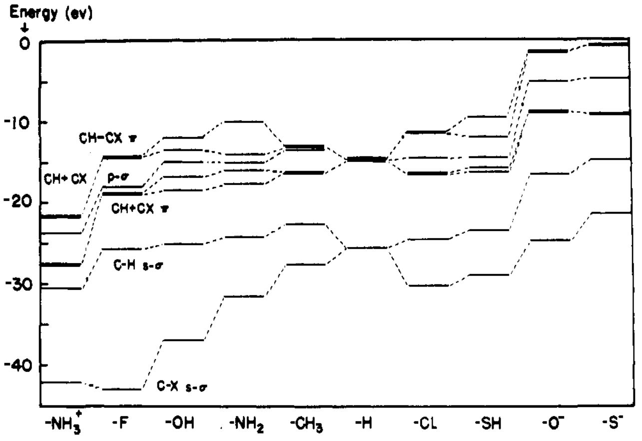

Figure 2. MO Energies for CH_3-X Compounds.

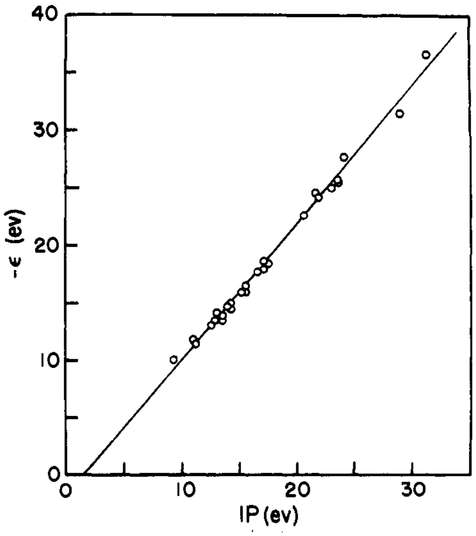

Figure 3. Correlation between ε and IP.

is developed. With both X = NH_3^+ and O^-, all energy levels are markedly perturbed.

The photoelectron spectra of many of these compounds have been examined and the ionization potentials determined.[8] It was previously found that the calculated molecular orbital energies for a series of alkenes were linearly related to the vertical ionization potentials, provided that a nonzero intercept was allowed.[9] The same is true in this case, and the correlation holds for both s- and p-type orbitals (Figure 3). The relation between the quantities is given by

$$-\mathrm{IP} = 0.83\epsilon - 1.5$$

This is essentially the same as that found for the alkenes.

The separation of the charge shifts into the σ and π components and the extension of these calculations to ethyl derivatives will be presented at a later time.

Acknowledgment. This investigation was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

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Photoselected Fluorescence Detected Circular Dichroism

Sir:

We report the first quantitative measurement of photoselected fluorescence detected circular dichroism (FDCD). In this measurement the optical activity of a chromophore is obtained by measuring the difference in fluorescence intensity for left and right circularly polarized excitation under conditions where rotation before emission is negligible. It was first pointed out by Ehrenberg and Steinberg that for these conditions the FDCD spectrum is not predicted by the simple theory of Turner et al.[1-3] Tinoco et al. subsequently developed a theory for this photoselected case.[4] According to this theory, the FDCD spectrum of the unoriented molecule can be obtained if a particular polarization of the fluorescence is detected. We have measured the FDCD spectrum of *10-d*-camphorsulfonic acid (CSA) and of morphine in glycerol and find reasonable agreement with this theory.

When the detector is perpendicular to the exciting light, and a linear polarizer is placed in front of it, the following expression can be derived for the measured FDCD signal when fluorophore rotation is negligible:[1,2,4]

$$\theta_{\mathrm{F}}^{\circ} = -14.32 \times \left[\frac{8R(1+\cos^2\phi) + (8R_{33}/3)(2-3\cos^2\phi)}{D(4-\cos^2\phi) - (D_{33}/3)(2-3\cos^2\phi)} - 2R_1\right] \quad (1)$$

ϕ is the angle that the detected polarization makes with the axis perpendicular to the excitation beam (i.e., when the polarizer is perpendicular to the excitation beam, $\phi = 0°$), R and D are the average rotational and dipole strengths, respectively, and R_{33} and D_{33} are the rotational and dipole strengths along the direction of the emission transition moment. The quantity R_1 is given by

$$R_1 = \frac{\Delta A}{2A} - \frac{2.303\Delta A \times 10^{-A}}{2(1-10^{-A})} \quad (2)$$

where A is the absorbance of the sample and ΔA is the absorbance for left circularly polarized light minus that for right circularly polarized light. Equation 1 predicts that the FDCD spectrum can be a function of polarizer angle and that $\theta_{\mathrm{F}}^{\circ} = -14.32(4R/D - 2R_1)$ when $\phi = 35.25°$. The values of $4R/D$ and R_1 can be obtained by measuring the circular dichroism (CD) and absorption spectra of the sample if only one species is present. Thus, comparison of the FDCD spectrum predicted

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